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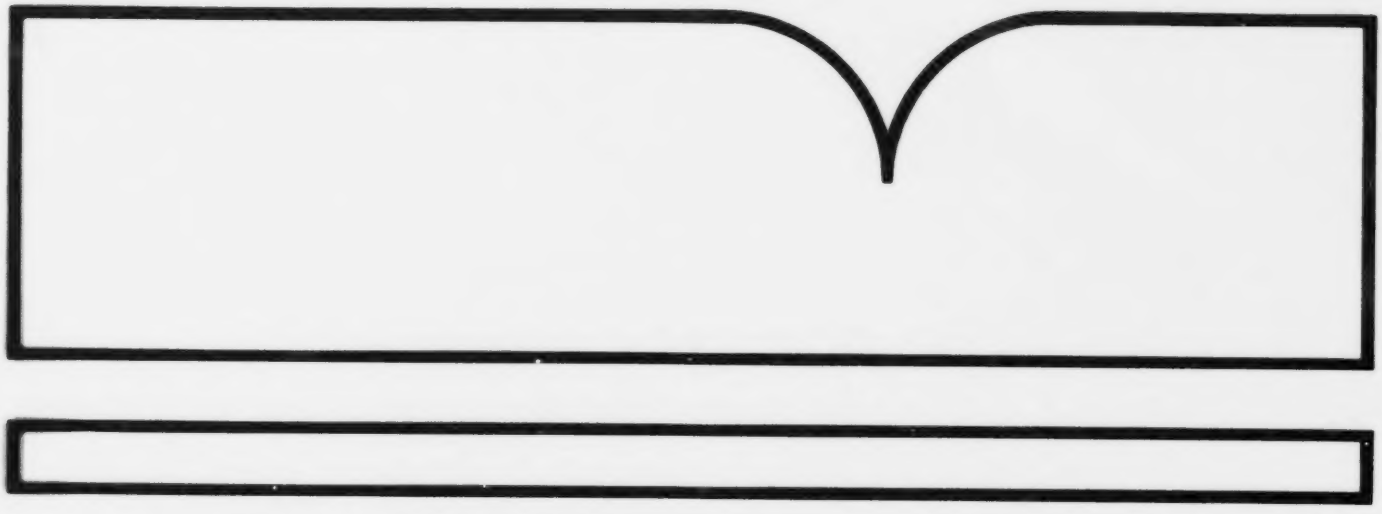

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16. ABSTRACT

The southwestern shoreline area of Lake Superior is subjected to extensive erosion of glacial-lacustrine red clay deposits. Clay bluff from the shoreline contains a large percentage of clay-size particles which remain suspended in Lake Superior for days to weeks. The clay-size particles undergo solubilization and exchange processes in the lake water. This investigation measures inputs of chemical parameters from clay particles in Lake Superior water as of a function of time. Comparisons of the chemical input magnitudes from shoreline erosion, sediment resuspension, and river particulate transport are made. Monitoring of Bayfield County, Wisconsin streams for sediment transport was done for the spring runoff period. The chemical characteristics of a near-shoreline Lake Superior site was studied as a function of water turbidity.

The results show that shoreline erosion is the principal mechanism for chemical transport to Lake Superior from clay particles as compared to stream particulate and sediment-resuspension inputs. The suspended particles have the capability of removing chemical species such as heavy metals and many organic chemicals from the aqueous phase. The sediment input from Bayfield County, Wisconsin streams is small compared to the input from streams of Douglas County, Wisconsin. Insufficient data was obtained to warrant conclusions on the field studies of turbidity and water chemistry relationships.

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CHEMICAL EFFECTS OF RED CLAYS ON WESTERN LAKE SUPERIOR

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FOREWORD

The U.S. Environmental Protection Agency (EPA) was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA was established in Region V, Chicago, to provide a specific focus on the water quality concerns of the Great Lakes. GLNPO provides funding and personnel support to the International Joint Commission activities under the U.S.-Canada Great Lakes Water Quality Agreement.

Several water quality studies have been funded to support the Upper Lakes Reference Group (ULRG) under the Agreement to address specific objectives related to pollution in the Upper Lakes (Lake Superior and Lake Huron). This report describes some of the work supported by this Office to carry out ULRG study objectives.

We hope that the information and data contained herein will help planners and managers of pollution control agencies make better decisions for carrying forward their pollution control responsibilities.

Dr. Edith J. Tebo
Director
Great Lakes National Program Office

PREFACE

This study was carried out during 1975 with the goal of providing information on the effects of red clay erosion on sediment transport and chemical inputs to Lake Superior. A draft final report was prepared in late 1975 at the conclusion of the project. A decision to publish this report was made in early 1978 at which time the authors commenced revisions. The report has been written in the context of information available at the beginning of 1976.

ABSTRACT

The southwestern shoreline area of Lake Superior is subjected to extensive erosion of glacial-lacustrine red clay deposits. Clay bluff from the shoreline contains a large percentage of clay-size particles which remain suspended in Lake Superior for days to weeks. The clay-size particles undergo solubilization and exchange processes in the lake water. This investigation measures inputs of chemical parameters from clay particles in Lake Superior water as of a function of time. Comparisons of the chemical input magnitudes from shoreline erosion, sediment resuspension, and river particulate transport are made. Monitoring of Bayfield County, Wisconsin streams for sediment transport was done for the spring runoff period. The chemical characteristics of a near-shoreline Lake Superior site was studied as a function of water turbidity.

The results show that shoreline erosion is the principal mechanism for chemical transport to Lake Superior from clay particles as compared to stream particulate and sediment resuspension inputs. The suspended particles have the capability of removing chemical species such as heavy metals and many organic chemicals from the aqueous phase. The sediment input from Bayfield County, Wisconsin streams is small compared to the input from streams of Douglas County, Wisconsin. Insufficient data was obtained to warrant conclusions on the field studies of turbidity and water chemistry relationships.

This report was submitted in fulfillment of Grant No. R005169-01 by the University of Wisconsin, Superior under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 1, 1974 to December 31, 1975 and the work was completed as of October 30, 1978.

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SECTION 1

INTRODUCTION

The water quality of western Lake Superior is directly affected by extensive erosion of glacial-lacustrine red clay deposits located primarily in northern Wisconsin. These clay deposits were formed in an early stage of present-day Lake Superior and now form a mantle of unconsolidated material averaging 100 feet (30 m) in depth. The depth increases westward from about 33 feet (10 m) near Port Wing, Wisconsin to more than 570 feet (174 m) at one point in the city of Superior, Wisconsin. The red clay drainage area of Wisconsin encompasses 890,000 acres (3600 km^2) located in Ashland, Bayfield, Douglas, and Iron counties.[1] Exposure of the red clay deposits occurs along 105 miles (169 km) of shoreline, of which 15% of the exposure has been classified by the Great Lakes Basin Commission as being under critical erosion. Eroded red clay is the major source of turbidity problems associated with rivers' draining the clay deposits and the shoreline area of southwestern Lake Superior. A considerable portion of the eroded material disperses into the water as fine particles (less than 2 microns) and thus forms suspensions of lengthy stability. The suspended material may be carried for long distances in Lake Superior before deposition on the bottom. The clay material which is deposited out to 70 feet (21 m) in depth is susceptible to resuspension during certain wind events, particularly when the southwestern part of the lake is under isothermal conditions (late spring and fall).[2,3]

The most pertinent information relating to the red clay input into the lake and its resuspension is contained in several available reports. Sydor[2,3] has examined the available data on red clay erosion into Lake Superior and concluded that the lake turbidity is primarily due to shore erosion and resuspension. Based on stream-monitoring data (see Section 8 for Bayfield County, Wisconsin data), measurements of fine suspended solids in the lake and particle-size distribution analysis of soil samples, Sydor concludes that the total stream erosion of soils amounts to 5.9×10^5 metric tons of material in Douglas County, of which 3.2×10^5 (or 54%) represents material which is carried into Lake Superior. The Nemadji River is the principle source of sediment load to Lake Superior, contributing 89% of the eroded material from streams in Douglas and Bayfield Counties. Rivers in Douglas and Bayfield Counties account for 80% of the Wisconsin Lake Superior tributary stream banks which are classified as under very severe or severe erosion.

The amount of eroded clay material entering Lake Superior due to shoreline erosive processes has been considered by Hess.[5] Using available aerial photographs in conjunction with shoreline observations, the recent rate of erosion is 2.5×10^6 cubic yards (1.9×10^6 m^3) per year for the coastal

area extending from Superior entry (Superior, Wisconsin) to Bark Point, a few miles west of Cornucopia, Wisconsin. This shoreline distance is slightly greater than 50 miles (80 km). Using a clay density of 120 lbs/cubic foot (1920 kg/m^3), the above volume of clay is equivalent to 3.7 x 10^6 metric tons. Hess estimates that this value accounts for somewhat less than half of the total erosion on Wisconsin's Lake Superior shoreline. Consequently, an estimate of the total eroded material along the shoreline is 8 x 10^6 metric tons per year. Sydor[3] has used ERTS images, settling rates, particle-size data, and lake sampling and arrived at a comparable figure in terms of erosion along the shoreline in Douglas County, Wisconsin. He determined that 2.3 x 10^6 metric tons of red clay is eroded from the shoreline in Douglas County. Since the Douglas County shoreline distance is slightly greater than one half the shoreline distance studied by Hess, the results of the two investigators are in good agreement.

Evidence that resuspension of fine sediment material from the lake bottom contributes significantly to lake turbidity is summarized by Sydor[2,3]. The available data now indicate that approximately 5.6 x 10^5 metric tons/year of lake-bottom sediment undergoes resuspension due to currents and in times of turbulent lake conditions in the shoreline regions of southwestern Lake Superior during the May-to-November period. An additional 10^6 metric tons/year is subject to resuspension during the December-through-April period. This accounts for a total yearly resuspension contribution to lake turbidity of 1.6 x 10^6 metric tons although this value includes material which has been disturbed more than once. Resuspension involves sediments deposited at depths up to 70 feet (21 m).

A major part of this study involves an investigation of the degree to which naturally occurring red clay material affects the concentrations of major and minor nutrients in this Lake Superior area. Some information on removal of organic pollutants by suspended clay particles constitutes a further phase of the project. Clay effects on water chemistry result from solubilization, exchange, and adsorptive processes. Representative clay-bearing material consisting of soil samples from shoreline and tributary clay banks, particulate material from the Nemadji River and Lake Superior have been employed in this chemical study. The major chemical parameters in aqueous systems investigated in this project included dissolved solids, dissolved oxygen, total Kjeldahl nitrogen, nitrate, total soluble phosphate, inorganic soluble phosphate, alkalinity, silica, sodium, potassium, magnesium, calcium, iron, manganese, zinc, copper, lead, nickel, chromium, selenium, arsenic, mercury, chloride, phenolics, chlorinated hydrocarbons, and PCBs.

Another phase of this project involved aiding Dr. Michael Sydor, University of Minnesota-Duluth, in determining with more accuracy the magnitude of tributary sediment-load discharge in Lake Superior by monitoring river spring runoff of suspended solids. Lake Superior monitoring in a high-turbidity region was done over the period from spring to the end of August in order to provide information on settling and transport of the suspended material and to obtain chemical data as related to turbidity and weather events.

The erosion of red clay results in property loss, turbidity in drinking water intakes, a decrease in aesthetic value of the southwestern shoreline

area of the lake, and some recognized adverse effects on fish life such as clogging of gravel beds necessary for fish reproduction and changing fish feeding habits, distribution, and mortality rates.[4]

It is the purpose of this study to determine the chemical effects of red clay erosion on the southwestern portion of Lake Superior through a study of the solubilization and sorptive properties of the clay materials in the forms of soils (clay bluff), river particulates, and sediments. In order to obtain meaningful results, information pertaining to the magnitudes of shoreline and river erosion and resuspension of clay sediments and the transport of the material must be known. Consequently this project is a cooperative effort with Dr. Michael Sydor, University of Minnesota-Duluth, whose research efforts are concentrating on determining magnitudes of the contributions of the erosion and resuspension factors to Lake Superior turbidity and the transport of the material in the lake (EPA Grant No. R005175-1).

SECTION 2

CONCLUSIONS

The erosion of red clay material results in inputs of many chemical parameters to the southwestern Lake Superior area. For those parameters considered in this study, chemical release from particles entering Lake Superior due to shoreline erosion of clay bluff is the largest source of chemical imputs (when compared to releases from river particulates and resuspension of sediments). The transport of river particulates to the lake and resuspension of bottom sediments during periods of high waves are secondary processes resulting in chemical releases to the lake.

Upon suspension of red clay containing bluff, sediment, and river particulate material in Lake Superior water, measurable releases of dissolved solids, total alkalinity, orthophosphate, total soluble phosphorus, and silica were found. The metals which are released in detectable quantities were sodium, potassium, calcium, magnesium, iron, aluminum, and manganese. Within the accuracy of the experiments, no detectable releases of chloride, TKN, nitrate, copper, cadmium, zinc, lead, chromium, nickel, mercury, arsenic, and selenium occurred. However, among the metals only potassium and calcium were studied for possible release from river particulates.

Suspended red clay bluff particles have the capacity for removing chemical species from Lake Superior water. Specific results on aqueous copper (II) and manganese (II) show that the suspended particles would remove copper from the water if its aqueous concentration reaches levels of about 1 µg/l or greater. Manganese removal by suspended bluff material from Lake Superior water would occur if its aqueous concentration increased to about 4 µg/l or more. The suspended clay particles also will remove phenolic type compounds from lake or river water.

The sediment load of rivers in Bayfield County, Wisconsin is small compared to the total sediment load of Douglas County, Wisconsin rivers.

SECTION 3

RECOMMENDATIONS

The magnitude of the chemical inputs to Lake Superior directly associated with release from eroded and resuspended red clay material should be compared to inputs from other water or airborne sources associated with anthopogenic activities.

The rate of dissolution of red clay bluff or sediment material in Lake Superior water should be determined from data in this report. In addition, sediment fluxes for a number of major chemical species should be computed.

The transport to Lake Superior of chemical species associated with suspended particulates and the bioavailability of these species should be investigated for metals and organic compounds. The large sediment load of the Nemadji River which passes through portions of the Duluth-Superior Harbor before entering Lake Superior should in particular be studied for chemical transport to the lake and its effect on the Lake Superior fishery.

SECTION 4

DISSOLUTION OF SOIL AND SEDIMENT SAMPLES

GENERAL PROCEDURES

Sediment and soil samples were collected for subsequent use in leaching and exchange experiments. The sediment samples were obtained using a Peterson dredge and placed in five-quart (4.7 l) plastic containers. The sealed containers were stored at approximately 4°C in the dark until their use in the leaching and exchange experiments. Soil samples were taken from exposed clay bluff deposits along the banks of the Bois Brule and Nemadji Rivers and from several locations along the shoreline of Lake Superior. These samples were also stored in five-quart plastic containers at room temperature. All soil samples except the Bardon Creek area samples were air-dried at room temperature before use in the experiments.

One river particulate sample consisting of suspended solids from the Nemadji River was used in the leaching-exchange studies. The sample was collected by filling 5-gallon (18.9 l) plastic carboys with Nemadji River water obtained with a Van Dorn water sampler. The water was put into four modified one-liter plastic polyethylene bottles and centrifuged for one hour at 2400 rpms (1,580 X g), at which point most of the suspended material had settled. The lower layer of the concentrated suspension was then filtered through 0.45 micron membrane filters. The filtered material was transferred to a pre-weighed plastic bottle with a plastic spatula. Approximately five minutes of filtering time was required per liter of river water processed. Approximately 35 liters of river water yielded 5 grams of wet solid material.

The sample locations, type of sample, and date collected are summarized in Table 1, and the sample locations have been indicated in Figure 1.

On the day of collection of the four sediment samples (SE-1, DS-1, AR-1 and SE-2), approximately one gram of each sample was added to one liter of Lake Superior water. The mixture was stirred for four months at room temperature. The water was then analyzed for dissolved oxygen, alkalinity, conductivity and pH while filtered portions (0.45 micron pore) were analyzed for calcium, magnesium, sodium, nitrate, chloride, silica, aluminum, cadmium, chromium, copper, iron, lead, manganese, arsenic, nickel, selenium and zinc. Most of the heavy metals were analyzed by both the EPA, Region V Laboratory, Chicago and the UWS laboratory. This experiment indicates which parameters might show larger concentration changes over long periods of time, although container adsorption or leaching effects would mask the true magnitudes of changes caused by clay-lake water interactions.

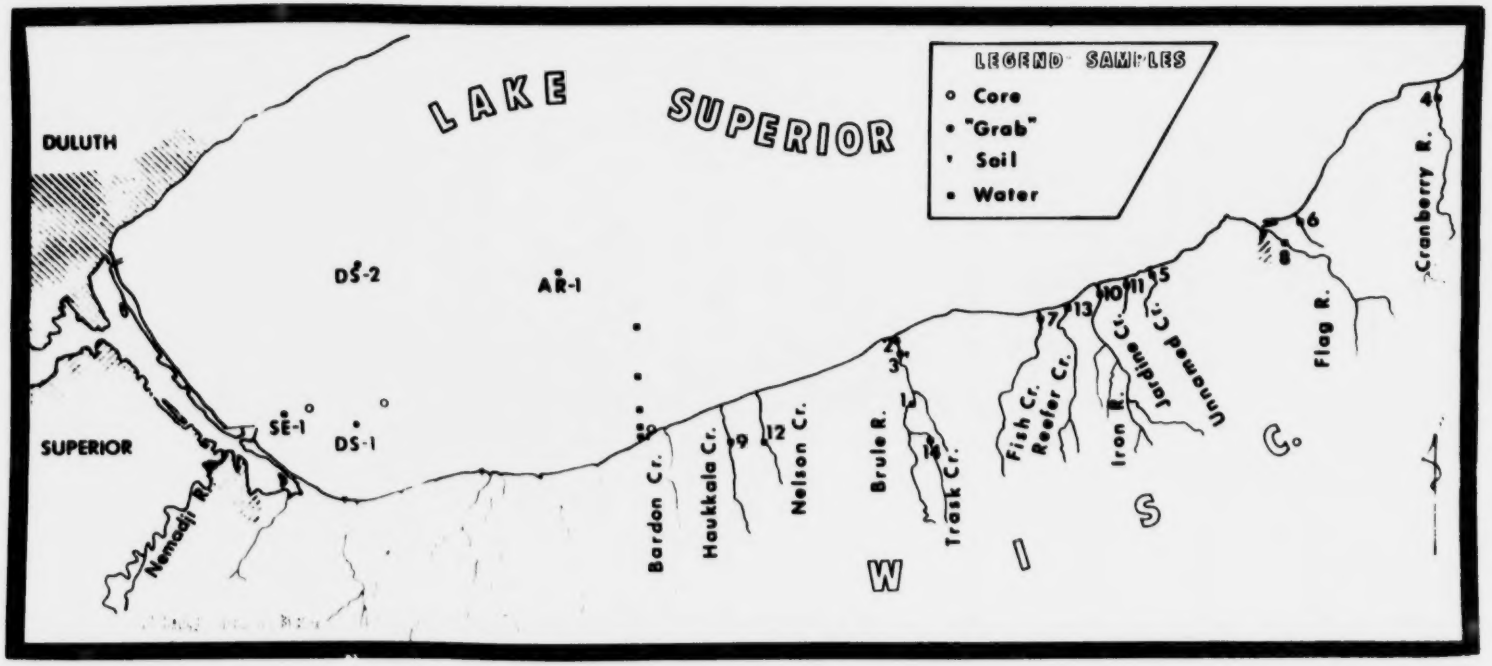

Figure 1. Sample collection points within study area.

TABLE 1: SEDIMENT AND SOIL SAMPLES

Designation	Sample Type	Sample Location	Date Collected
SE-1	Sediment	3/4 mile from Superior entry lighthouse (60-foot depth)	12/14/74
DS-1	Sediment	2-1/3 miles from the mouth of Dutchman's Creek (60-foot depth)	12/14/74
AR-1	Sediment	6-2/3 miles from the mouth of the Amnicon River (125-foot depth)	12/14/74
DS-2	Sediment	7-1/3 miles from the mouth of Dutchman's Creek	12/14/74
B-1	Soil	North of Highway 13 near fisherman's parking lot on banks of Bois Brule River	12/6/74
B-2	Soil	Bois Brule River banks 40 feet to north of B-1	12/6/74
N-1	Soil	200 yards upstream of Woodland Road bridge on the banks of the Nemadji River	12/6/74
N-2	Soil	Nemadji River banks 15 yards upstream of N-1	12/6/74
LS-1	Soil	Lake Superior shoreline 100 yards west of the mouth of the Amnicon River (gray clay)	12/6/74
LS-2	Soil	Lake Superior shoreline 20 yards west of LS-1 from the face of eroded cliff	12/6/74
LS-3	Soil	Lake Superior shoreline taken below LS-2 on the same cliff	12/6/74

TABLE 1: SEDIMENT AND SOIL SAMPLES (CONTINUED)

Designation	Sample Type	Sample Location	Date Collected
LS-4	Soil	Lake Superior shoreline exposed clay bank 150 yards west of the mouth of Dutchman's Creek	12/6/74
LS-5	Soil	Lake Superior shoreline exposed clay bank 15 yards west of LS-4	12/6/74
BC-1	Soil	Lake Superior shoreline one mile west of Bardon Creek 50 feet above shoreline	6/4/75
BC-2	Soil	Lake Superior shoreline one mile west of Bardon Creek 5 feet above shoreline	6/4/75
BC-3	Soil	Lake Superior shoreline 20 yards east of BC-2 just above the sand beach	6/4/75
NP-1	River Particulate	Nemadji River water sample obtained at Woodland Road bridge site	6/4/75

Two seven-week leaching experiments were performed using soil or sediment samples in Lake Superior or distilled water using a procedure similar to that used by Plumb.[6] The aqueous suspensions were equilibrated under various conditions with respect to temperature, pH, dissolved oxygen, and degree of agitation. The general procedure for soils consisted of using approximately five grams of the air-dried soil sample in 10 liters of water in a Pyrex container. Small chunks of each clay sample were placed on a #230 standard sieve (62.5μ pore) and spray washed through the sieve using lake water. The clay-water suspension was rinsed into the 10-liter flask and an appropriate amount of water was added to bring the water volume to 10 liters. The residue and sieves were dried at 115°C for one hour and the weight of residue was determined. This procedure removed the sand-size particles from the sample and allowed a calculation of the weight of silt-clay size material in the flasks. Blanks containing only Lake Superior or deionized water were also prepared. One liter of the water sample was removed by siphoning (after allowing some settling of particles for stirred samples). The siphoning was performed using glass tubing in the apparatus and was begun employing a short spurt of purified air from an oil-less, dried, filtered, compressed air source. After removing one liter of water, an additional liter of Lake Superior water was added to bring the water volume back to 10 liters. The lake water used was obtained from the lake intake at the Environmental Research Laboratory (ERL), Duluth, Minnesota. This experiment was conducted at room temperature (23 to 28°C).

For the net removal and addition of one liter of water, 1.065 liters of water was removed. Of this 1.065 liters, 65 ml was directly siphoned into a 65 ml dissolved oxygen bottle with the remaining liter put into a plastic container. The one liter was centrifuged at approximately 2400 rpms (1,580 X g) for approximately 30 minutes and 945 ml of the supernatant was siphoned at the ERL for analysis. The remaining 65 ml, which contained the large majority of the suspended material, was returned to the leaching flasks along with 1 liter of lake water. Most of the supernatant liquid was then filtered through either 0.1 micron or 0.45 micron membrane filters. Any suspended material on the filters was rinsed back into the leaching flasks with part of the liter of water. Of the 945 ml of water sample, approximately 150 ml was not filtered, this portion being used for conductivity and alkalinity measurements. The sample blanks were also subjected to the water removal and addition procedure. The Lake Superior water used in portions of the experiments was filtered before addition to the flasks. The water referred to as "distilled" was purified by passing tap water through a reverse osmosis, adsorption-ion exchange process (Milli Q-2, Q-3 systems).

The experiments involving Lake Superior sediments were carried out using procedures identical to those enumerated for the soil samples with the following modification. The sediment samples were not dried but moist subsamples were weighed, divided in half, and one half of the sample was wet-sieved into the flask. The other half of the sub-sample was dried at 100-105°C for a dry weight determination.

Low-oxygen water conditions were obtained by flushing the water for 20 minutes with pre-purified N_2, employing a gas dispersion tube and N_2 flushing of the space above the solutions. Lowering the pH of certain of the solutions was accomplished by saturating the water with CO_2 and monitoring the pH upon removing a sample for analysis. The leaching at 4°C was performed in a constant temperature room at the ERL, Duluth.

The parameters measured in the aqueous suspensions as a function of time were total Kjeldahl nitrogen, orthophosphate, total soluble phosphorus (phosphorus contained in a sample after it has been filtered through a 0.45 micron filter and digested in acid), nitrate, chloride, alkalinity, calcium, magnesium, potassium, sodium, and conductivity. In addition, measurements of temperature, pH, and dissolved oxygen were made. Analyses for these parameters were performed at the initiation of the experiments and one day, one week, three weeks, five weeks, and seven weeks after initiation. The samples and conditions used in these leaching experiments are listed in Table 2.

The clay-to-solution ratio used in these seven-week leaching experiments (5 grams per 10 liters of water) result in suspended solid concentrations which are of the same magnitude (500 mg/l) as could occur in Lake Superior following intense weather events in the shoreline area. Tributary rivers reach suspended solid concentrations of 1000 mg/l for brief times during high-flow periods. Using a higher clay-to-solution ratio could result in changes in the relative particle-size distributions toward higher percentages of larger particles. Consequently the 500 mg/l suspensions were used. However, changes in the values of some of the parameters with time were small (particularly sodium, potassium, magnesium, and calcium). Consequently, the errors associated with the analytical determinations of these parameters resulted in large uncertainties in their release magnitudes from the clay. In order to achieve greater aqueous concentration changes in these parameters with time [and decrease the per cent uncertainty in the parameter release values as computed by equation (1)], the clay-to-solution weight ratio was increased in a separate dissolution study. Two samples were used in this leaching experiment, namely LS-5 (soil) and the upper layer of the Dutchman's Creek-area core sample (sediment) as described in Section 5 of this report. The clay-to-solution ratio was approximately one gram per 500 ml of lake water or 2000 mg/l. The clay samples were weighed into separate polypropylene one-liter containers. Twelve "identical" suspensions for both the soil and sediment sample, along with six lake-water blanks, were prepared. Duplicate suspensions of the soil and sediment samples were analyzed after one day, one week, three weeks, five weeks, seven weeks and nine weeks. In preparing the suspensions, the clay samples were wet-sieved into the sample containers to remove sand-size particles and, in the case of the sediment suspemsions, they were prepared under a nitrogen atmosphere in a dry box, thus preventing exposure of the sediment to air in the atmosphere. The suspensioms were agitated by periodically shaking the plastic containers.

In addition, a three-month separate leaching study was carried out for silica, using plastic containers. The clay-solution ratio for the suspensions was approximately 2000 mg/l. The suspensions were leached under both

TABLE 2: SAMPLES AND CONDITIONS FOR SEVEN-WEEK LEACHING EXPERIMENTS*

Sample Number	Sample	Conditions**
1	B-2 Soil	high O_2, stirred
2	B-2 Soil	high O_2, stirred
3	N-1 Soil	high O_2, stirred
4	N-1 Soil	high O_2, stirred
5	LS-1 Soil	high O_2, stirred
6	LS-1 Soil	high O_2, stirred
7	LS-5 Soil	high O_2, stirred
8	None	high O_2, stirred
9	SE-1 Sediment	high O_2, stirred
10	SE-1 Sediment	high O_2, stirred
11	DS-1 Sediment	high O_2, stirred
12	None	high O_2, unstirred
13	N-1 Soil	high O_2, unstirred
14	N-1 Soil	high O_2, unstirred
15	LS-5 Soil	high O_2, unstirred
16	LS-5 Soil	high O_2, unstirred
17	None	high O_2, stirred
18	NP-1 Particulate	high O_2, stirred
19	LS-5 Soil	high O_2, stirred
20	LS-5 Soil	high O_2, stirred
21	None	high O_2, stirred
22	DS-1 Sediment	low O_2, stirred
23	LS-5 Soil	low O_2, stirred
24	None	low O_2, stirred
25	LS-5 Soil	low pH, high O_2, unstirred
26	LS-5 Soil	low pH, high O_2, unstirred
27	DS-1 Sediment	low pH, high O_2, stirred
28	None	low pH, high O_2, unstirred
29	LS-5 Soil	high O_2, stirred, 4°C
30	LS-5 Soil	high O_2, stirred, 4°C
31	DS-1 Sediment	high O_2, stirred, 4°C
32	None	high O_2, stirred, 4°C

*Clay-to-solution ratio is approximately 500 mg/l.

**All samples run at room temperature (23 to 27°C) at the normal pH of lake water or deionized water unless indicated otherwise. Lake Superior water was used in all systems except for sample numbers 19, 20, and 21, for which deionized water was used.

high - oxygen and low-oxygen water conditions employing both Lake Superior water and deionized water as the leaching media. The conditions and samples used in this study are summarized in Table 3.

RESULTS AND DISCUSSION

Four-Month Preliminary Leaching Experiments

The results of the four-month leaching study are shown in Table 4. This study was intended as a longer-term leaching experiment on sediments to give some estimate of those parameters which may be expected to show larger concentration changes in Lake Superior waters over this time period. The lake water was not analyzed at the initiation of the experiment, and no Lake Superior water blank was run concurrently with the samples. In addition, adsorption affects on the walls of the containers might seriously affect concentrations particularly of the soluble heavy metals. The values reported here have not been used in any of the calculations of inputs given in this report. However, since these data may be of some general interest, the values have been tabulated. It can be conjectured from these data that increases in alkalinity and specific conductance occurred particularly for samples SE-1 and DS-1. The values of specific conductance for samples SE-1 and DS-1 had increased from the values normal for Lake Superior water by approximately 35 micromhos/cm, which is equivalent to about 21 mg/l of dissolved solids. The lake water in contact with sediment samples AR-1 and DS-2 showed lower oxygen content, perhaps indicative of the presence of larger amounts of oxygen-demanding material, although the 13.4 mg/l oxygen value for SE-1 is certainly questionable. Silica exhibited a three to sixfold increase in the four leaching systems.

Seven-Week Leaching Experiments

The data for the seven-week leaching experiments pertaining to the systems summarized in Table 2 was treated by calculating the total release of the particular parameter from the clay material with time (when applicable). Using a leaching water volume of ten liters and noting that one liter of water is removed and a new liter of water (lake or deionized) is added for each analysis time, the total release in milligrams or micrograms is calculated by equation (1):

$$R_n = 10\,1\,[X_n - X_o{}^1] + 1.0\,1\,\left[\sum_{i=1}^{i=n-1} X_i - \sum_{i=1}^{i=n-1} X_i{}^1\right] \quad (1)$$

where X_n = concentration of the parameter in mg/l or ug/l in the leaching water for the nth analysis

$X_o{}^1$ = initial concentration of the parameter in the leaching water at zero time

X^1 = concentration of the parameter in the one liter of water added on the day of analysis

TABLE 3: SAMPLES AND CONDITIONS FOR SILICA-LEACHING STUDIES*

Sample Number	Sample	Conditions**	Leaching Water Type
1	SE-1 sediment	high O_2, unstirred	Lake Superior Water
2	SE-1 sediment	high O_2, unstirred	Lake Superior Water
3	SE-1 sediment	low O_2, unstirred	Lake Superior Water
4	SE-1 sediment	low O_2, unstirred	Lake Superior Water
5	None	low O_2, unstirred	Lake Superior Water
6	SE-1 sediment	high O_2, stirred	Lake Superior Water
7	SE-1 sediment	high O_2, stirred	Lake Superior Water
8	SE-1 sediment	low O_2, stirred	Lake Superior Water
9	SE-1 sediment	low O_2, stirred	Lake Superior Water
10	None	low O_2, stirred	Lake Superior Water
11	LS-5 soil	high O_2, stirred	Lake Superior Water
12	LS-5 soil	high O_2, stirred	Lake Superior Water
13	None	high O_2, stirred	Lake Superior Water
14	LS-5 soil	high O_2, unstirred	Lake Superior Water
15	LS-5 soil	high O_2, unstirred	Lake Superior Water
16	None	high O_2, unstirred	Lake Superior Water
17	LS-5 soil	high O_2, stirred	Deionized Water
18	LS-5 soil	high O_2, stirred	Deionized Water
19	None	high O_2, stirred	Deionized Water

*Clay-to-solution ratio is approximately 2000 mg/l.

**All samples run at room temperature (23 to 27°C) and at the normal pH of lake water or deionized water.

TABLE 4: FOUR-MONTH CLAY SEDIMENT LEACHATE RESULTS

Sample*	Copper (µg/l)	Aluminum (µg/l)	Cadmium (µg/l)	Chromium (µg/l)
SE-1	7	<100	1.0	0.8
DS-1	4	<100	0.2	1.3
AR-1	7	<100	0.2	0.3
DS-2	8	<100	0.2	0.3

Sample	Iron (µg/l)	Lead (µg/l)	Manganese (µg/l)	Nickel (µg/l)	Zinc (µg/l)
SE-1	28	<1	1.4	<20	12
DS-1	20	<1	0.8	<20	7
AR-1	20	<1	1.0	<20	6
DS-2	32	<1	1.4	<20	6

Sample	PO_4 (µg PO_4/l)	Total Soluble P (µg P/l)	D. O. (mg/l)	Alkalinity (mg $CaCO_3$/l)	Specific Conductance
SE-1	6	5	13.4	58.9	132
DS-1	4	7	10.2	58.3	131
AR-1	5	5	5.6	50.3	93
DS-2	4	3	5.8	54.2	114

Sample	pH	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Chloride (mg/l)	Silica (mg SiO_2/l)
SE-1	7.63	12.4	4.5	1.9	2.3	13.4
DS-1	7.52	13.3	4.5	1.8	1.6	8.0
AR-1	7.10	7.8	3.0	1.7	1.9	12.4
DS-2	7.59	11.5	3.7	1.9	1.6	7.9

*Suspension concentrations are: SE-1 = 2.51 g/l, DS-1 = 3.19 g/l, AR-1 = 1.74 g/l and DS-2 = 2.43 g/l on a wet basis.

and R_n = total release in milligrams or micrograms for the nth analysis

In order to correct for changes in the values of a particular parameter with time due to effects not associated with clay interactions (such as leaching from the walls or adsorption from the container walls), R_n values were computed for the blanks containing no clay samples. The appropriate R_n blank value was subtracted from the R_n value of the parameter in the clay-water systems at the same conditions as the blank. The resulting difference was divided by the dry weight of the clay sample and these values tabulated in mg or ug of the parameter released per gram of the clay samples as a function of time. The data was grouped according to all samples leached for each parameter. This data along with the pH, specific conductance, and dissolved oxygen versus time values are listed in Tables A-1 through A-14 in Appendix A. Summaries of the data for leaching the soil, sediment, and river particulate samples at two leaching times (one day and seven weeks) are given in Tables 5 and 6.

Similarly, the total corrected release values for the silica-leaching experiments (Table 3) were computed and tabulated in Table 7. The additional experiment involving leaching of one clay soil and one clay sediment sample in plastic containers at solid-to-solution ratios of about 2000 mg/l are listed in Table 8 in terms of total corrected releases. These results will be summarized according to the changes found for each parameter as tabulated in these tables.

Dissolved Solids--

The amount of dissolved solids in the soil-water systems progressively increased with time under all conditions. The amount of dissolved solids increase was twice as large under highly oxygenated water conditions compared to low-oxygen conditions. Lowering the pH to approximately 5.5 (from the normal pH of Lake Superior water) resulted in a sixfold increase in dissolved solids. Twice as much solid material dissolved from soil samples in deionized water as found for Lake Superior water. Temperature had only a small effect on the amount of dissolved solids.

The sediments released smaller amounts of dissolved solids in water than the soil samples. In particular, the sediments did not show the large initial dissolution of solids as exhibited by the soils, but a steady dissolution with time did occur. However, under low-oxygen water conditions, no release of solids from the sediments was detected. Release of dissolved solids from the Nemadji River particulate sample was similar to that found for soil samples.

Alkalinity--

Soil samples exhibited alkalinity releases equivalent to 12 to 140 mg of $CaCO_3$ per gram depending on conditions. The samples at a low pH gave the greatest releases while leaching under low-oxygen water conditions gave the smallest. When deionized water was used as the leaching agent in place of Lake Superior water, the alkalinity increase was more than doubled. Alkalinity release was the same within experimental error at 4°C as at room temperature.

TABLE 5: SUMMARY OF CLAY SOIL-WATER CHEMICAL EXCHANGES* IN MG OF PARAMETER PER G OF CLAY

Samples	1 through 7		13 through 16		19 and 20		23		25 and 26		29 and 30	
Conditions	Stirred, high O_2, Lake Superior water, 23-26°C		Unstirred, high O_2, Lake Superior water, 23-26°C		Stirred, high O_2, Deionized water, 23-26°C		Stirred, low O_2, Lake Superior water 23-26°C		Unstirred, high O_2, lower pH, Lake Superior water, 23-26°C		High O_2, stirred Lake Superior water, 4°C	
Leaching Time	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks
Parameter												
Dissolved Solids	12.3 (1.0)	24.4 (2.0)	10.6 (0.6)	23.8 (0.2)	42.6 (0.5)	61.0 (0.9)	6.7	12.2	87.4 (5.9)	139.1 (8.3)	15.9 (0.02)	30.0 (15.2)
Alkalinity	11.7 (1.6)	23.2 (1.5)	7.6 (0.6)	20.2 (0.8)	32.8 (1.8)	50.9 (1.6)	7.6	14.1	79.4 (1.2)	139.5 (6.8)	14.6 (1.6)	33.5 (9.6)
Orthophosphate (PO_4)	.029 (.008)	.016 (.008)	0.022 (0.006)	0.033 (0.009)	0.056 (0.007)	0.042 (0.002)	0.027	0.029	0.067 (0.005)	0.063 (0.010)	0.015 ($2x10^{-5}$)	0.032 (0.0004)
Total Soluble P	0.008 (0.005)	0.036 (0.021)	0.010 (0.003)	0.009 (0.004)	0.023 (0.021)	0.013 (0.002)	0.008	0.004	0.017 (0.014)	0.014 (0.015)	0.014 (0.003)	0.012 (0.003)
Nitrate	0.03 (0.07)	0.06 (0.15)	0.03 (0.08)	-0.06 (0.13)	0.19 (0.04)	0.13 (0.007)	-0.12	-0.98	0.18 (0.11)	0.15 (0.04)	-0.10 (0.17)	0.14 (0.06)
Chloride	0.41 (0.30)	0.27 (0.72)	-0.40 (0.18)	-0.29 (0.21)	0.06 (0.04)	-0.47 (0.28)	-0.21	-0.12	0.21 (0.14)	-0.08 (0.02)	-0.09 (0.03)	-0.14 (0.11)
Total Kjeldahl N	0.12 (0.06)	-0.02 (0.07)	0.04 (0.03)	----- -----	-0.25 (0.03)	----- -----	-0.14	-----	0.03 (0.04)	0.14 (0.06)	-0.06 (0.03)	-0.01 (0.24)
Sodium	0.24 (0.11)	0.23 (0.65)	0.16 (0.11)	0.38 (0.12)	0.14 (0.11)	0.74 (0.00)	0.10	0.79	0.41 (0.18)	-0.03 (0.26)	0.47 (0.03)	0.34 (0.02)
Potassium	0.41 (0.04)	0.42 (0.15)	0.33 (0.12)	0.16 (0.02)	0.40 (0.00)	0.45 (0.08)	0.29	0.11	0.32 (0.03)	0.37 (0.02)	0.15 (0.01)	0.58 (0.42)
Calcium	1.52 (0.67)	6.13 (1.40)	2.13 (0.80)	3.89 (2.56)	10.41 (0.16)	16.16 (0.30)	2.30	2.64	20.27 (3.11)	26.24 (2.86)	3.19 (0.72)	6.85 (3.13)
Magnesium	0.80 (0.51)	0.92 (0.39)	0.93 (0.27)	1.12 (0.13)	2.49 (0.06)	3.45 (0.02)	0.94	0.51	2.17 (0.06)	2.65 (0.08)	0.98 (0.04)	1.04 (0.09)

*Positive values denote release from the clay while negative values indicate uptake by the clay. Values in parentheses represent standa deviations. See Table 2 for sample identification.

TABLE 6: CLAY SEDIMENT AND RIVER PARTICULATE CHEMICAL EXCHANGES IN MG OF PARAMETER PER G OF CLAY

Samples*	9 through 11		22		27		31		18	
Conditions	Stirred sediment, high O_2, Lake Superior water, 23-27°C		Stirred sediment, low O_2, Lake Superior water, 23-27°C		Stirred sediment, low pH, high O_2, Lake Superior water, 23-27°C		Stirred sediment, high O_2, Lake Superior water, 4°C		Nemadji River particulate, stirred, high O_2, Lake Superior water, 23-27°C	
Leaching Time	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks	One Day	7 Weeks
Parameter										
Dissolved Solids	0.41 (0.36)	12.8 (1.6)	-3.0	-1.8	15.5	19.4	0.5	1.8	1.7	39.4
Alkalinity	0.51 (1.41)	10.3 (0.8)	-2.1	+2.2	19.3	26.5	-1.2	2.9	0.5	34.8
Orthophosphate	0.016 (0.014)	0.063 (0.027)	0.004	0.063	0.074	0.079	0.011	0.028	0.043	0.132
Total Soluble P	0.006 (0.005)	0.023 (0.002)	0.011	0.014	0.033	0.028	0.011	0.007	0.048	0.042
Nitrate	0.15 (0.04)	0.38 (0.19)	-0.10	-0.43	0.26	0.02	-0.24	0.04	0.05	3.1
Chloride	-0.63 (0.62)	-0.21 (0.11)	0.01	-0.20	0.46	-0.15	-0.12	-0.14	0.80	0.37
Total Kjeldahl N	0.01 (0.06)	-----	-0.21	-----	0	0.24	-0.07	-0.30	-0.11	0.48
Sodium	0.20 (0.17)	0.97 (0.32)	-0.14	0.54	-0.04	0.46	0.51	0.18	0.19	0.10
Potassium	0.06 (0.06)	0.24 (0.11)	0.20	0.24	0.15	0.40	0.03	0.21	0.24	0.24
Calcium	-0.097 (0.37)	-0.54 (2.65)	-0.70	-0.84	7.6	3.6	0.28	-0.98	0	1.6
Magnesium	0.14 (0.13)	1.89 (0.25)	0.02	-0.27	1.37	1.47	0.17	0.51	0.34	1.37

*See Table 2 for sample identification.

TABLE 7: TOTAL CORRECTED RELEASE OF SILICA IN MG OF SiO_2 PER G OF CLAY

Days Leached	1	8	15	22	36	44	53	64	78	93
Sample*										
1	0.04	0.22	0.51	0.84	0.90	1.29	1.29	1.95	2.31	2.82
2	0.01	0.15	0.47	0.72	1.18	1.19	1.56	1.98	2.30	2.84
3	0.11	0.79	0.93	1.01	1.35	0.92	1.09	2.22	2.36	3.15
4	0.15	0.40	0.88	0.96	1.30	1.65	2.02	2.32	2.32	2.88
6	-0.01	0.61	0.46	0.81	1.05	0.97	1.03	1.44	1.17	2.41
7	0.07	0.41	0.46	0.42	1.12	1.09	1.08	1.47	1.63	2.47
8	0.16	0.34	0.72	0.75	1.02	1.34	1.32	2.16	2.57	3.18
9	0.14	0.74	0.67	0.75	1.17	1.04	1.62	1.83	2.06	2.39
11	0.56	0.70	1.20	1.14	1.53	1.68	1.31	1.54	1.62	1.82
12	0.72	1.18	1.21	1.07	1.52	1.38	1.46	1.55	1.75	1.74
14	0.61	0.31	0.99	1.04	0.99	1.19	1.24	1.26	1.51	1.41
15	0.51	0.47	0.97	0.96	0.94	1.21	1.14	1.28	1.48	1.32
17	----	----	1.17	1.32	1.45	1.69	1.69	1.91	2.10	2.28
18	----	----	1.18	1.48	1.44	2.02	1.89	2.22	2.52	2.61

*Samples and Experimental conditions are described in Table 3.

TABLE 8: TOTAL CORRECTED CHEMICAL EXCHANGES FROM CLAY SOIL AND SEDIMENT SAMPLES

A. Sample: LS-5 Soil Sample in Lake Superior Water

	CHEMICAL EXCHANGES (mg parameter/g of clay)					
Days Leached	1	7	21	35	49	63
Calcium	-0.52	1.13	0.70	1.94	1.65	1.49
Magnesium	0.55	0.35	0.38	0.50	0.46	0.71
Sodium	0.15	0.14	0.11	0.15	0.17	0.18
Potassium	0.17	0.20	0.18	0.20	0.21	0.20

B. Sample: Lake Superior Sediment - Upper Layer of Dutchman's Creek-Area Sediment in Lake Superior Water

	CHEMICAL EXCHANGES (mg parameter/g of clay)					
Days Leached	1	7	21	35	49	63
Calcium	-0.24	0.11	-0.17	0.58	0.79	0.58
Magnesium	0.05	0.13	0.18	0.30	0.26	0.36
Sodium	0.05	0.04	-0.04	0.04	0.06	0.07
Potassium	-0.02	0.05	0.05	0.12	0.13	0.05

Sediments in water under the same conditions as the soils gave smaller alkalinity releases. Little or no alkalinity change was found in Lake Superior water under low-oxygen conditions. A smaller increase in alkalinity was found at a lower temperature (4°C) but this conclusion is based on only one sample. The alkalinity release for the Nemadji River particulate sample was larger than that found for soils.

Orthophosphate and Total Soluble Phosphorus--

The releases of orthophosphate amounted to 20 to 40 micrograms of PO_4 per gram of solid for soils in Lake Superior water. A rapid initial release occurred followed by a possible slight decline after a time of about one day. Use of deionized water in place of Lake Superior water resulted in increased releases as did lowering the pH. Little effect was noted with temperature or oxic conditions of the water. A more detailed study of the soil-orthophosphate systems is given in Section 6. The release values for total soluble phosphorus showed more scatter than the orthophosphate data with time. Releases ranged from 10 to 60 micrograms of phosphorus per gram of soil under Lake Superior conditions. An apparent lower release was noted under low-oxygen conditions with no definite conclusions possible from the data on pH and temperature effects.

Sediment releases of soluble phosphorus are comparable to those for soils (10 to 25 micrograms of P per gram of sediment) under normal Lake Superior water conditions. Lowering the pH increased the release somewhat. The Nemadji River particulate sample gave a larger release than any of the soil or sediment samples (about 70 micrograms of P per gram of particulate matter). The orthophosphate release was greater for sediment samples than for soil samples with the release occurring over a longer time period. A lower pH increased the rate and total release of orthophosphate. The pH effect on total phosphorus release is inconclusive due to the scatter in the data. The Nemadji River particulate sample gave the largest orthophosphate release (about 150 micrograms of PO_4 per gram of particulate matter) over the seven-week period. This larger release is discussed further in Section 6.

Nitrate--

The data in Appendix A show that the release values for nitrate are small. Under well-oxygenated Lake Superior water conditions, soil samples tended to show some release of nitrate on the order of 0.1 mg of NO_3 per gram of soil. Under low-oxygen water conditions a loss of nitrate from the lake water was found. The scatter in the release values for the sediment samples results in no definite conclusions except that the nitrate exchange is relatively small. The Nemadji River particulate sample showed a comparatively large net release of nitrate on the order of 3 mg of NO_3 per gram of particulate material.

Chloride--

As for nitrate, there is little change in chloride with time within the experimental accuracy as reflected in the fluctuations in the release values. It is concluded that soils have little effect on the chloride concentrations in Lake Superior water. The values listed for samples 1 through 7 in Table 5 are influenced by a relatively large release for sample 1 which may have

been contaminated. If this sample is ignored, the data indicates a total release of chloride of less than one mg per gram of clay. Sediment-water exchange of chloride was also small.

Total Kjeldahl Nitrogen--

The data indicate clay effects on the ammonia and organic nitrogen levels in Lake Superior were small. The low levels of ammonia and organic nitrogen in the lake water cause difficulty in detecting removal of organic material containing nitrogen. Experiments carried out at higher concentration levels of the nitrogen-containing compounds would be necessary to indicate the occurrence of clay adsorption or decomposition at the particle surface. There was no indication of organic containing nitrogen being released by the soil or sediments at levels above 0.2 mg of N per gram of clay.

Sodium and Potassium--

Although the data for sodium shows more scatter than that for potassium, the results show that both sodium and potassium are released from the clay soils. The release was relatively rapid in the case of soils and the concentrations of these parameters in lake water assumed steady values after the first day of leaching. The average release of sodium for the soil samples is 0.23 mg of Na per gram of soil for the 500 mg/1 suspensions. A greater release was found in deionized water (about 0.7 mg per gram of soil). The data for the one sample under low oxygen conditions was inclusive. A somewhat smaller release was shown in Table 8 for the 2000 mg/1 suspensions. This decrease in release with increase in clay-to-solution ratio is also seen for potassium, calcium, and magnesium. This may result from a greater exposed surface area per gram of clay in the lower clay-water ratio suspensions due to a smaller degree of particle flocculation. The release of potassium was somewhat higher than that for sodium. Thus a 0.4 mg of potassium per gram of clay soil was recorded for the 500 mg/1 suspensions and about 0.2 mg released in the 2000 mg/1 suspensions. Little or no difference was found for potassium release in deionized water as compared to Lake Superior water. A smaller release was indicated under low-oxygen conditions (only one sample) while lowering the pH had little effect on potassium release from soils.

The data in Table 6 for sodium release from sediments is inconclusive because of large variations in the releases with time. However, the data in Table 8 show a smaller release for sodium in sediments than soils (0.07 mg or less of sodium per gram of sediment). Similarly, potassium exchange values were smaller for the sediments (about 0.2 mg of potassium for 500 mg/1 and 0.1 mg of potassium for 2000 mg/1 suspensions). Release of potassium from the Nemadji River particulate sample was similar in magnitude to that for sediments.

Calcium--

The data indicate an approximate release of 6 mg of calcium per gram of soil in Lake Superior water (500 mg/1 suspensions). This value is two to three times greater in deionized water and lower under low-oxygen conditions. A lower pH caused a greater flux of calcium to the solution (about 25 mg of Ca per gram of soil). No significant difference was found with changing temperature.

The sediment data showed a much smaller release and possibly a removal of calcium from solution although the results are not conclusive. Data in Section 5 indicate some flux of calcium from sediments to the lake water. The Nemadji River particulate sample released less than 6 mg of Ca per gram of particulate material.

Magnesium--

Lake Superior water removed about 0.9 mg of Mg per gram of soil in the 500 mg/l suspensions while a removal of about 0.6 mg occurred in the 2000 mg/l suspensions. The release is quadrupled in deionized water (about 3.4 mg of Mg) but little difference is shown for changes in oxygen content of the water. A lower pH (about 5.5) triples the release in lake water. A temperature change from about 25°C to 4°C shows no detectable effect.

The data in Table 6 indicates a greater release for sediments than soils but the data in Table 8 shows a smaller release. We conclude that the sediments do provide magnesium to the lake water in the range of 0.5 to 2.0 mg of Mg per gram of dry sediment for the 500 mg/l level and the magnitude of the release is still increasing after seven weeks. The Nemadji River particulate sample releases 1.0 to 1.5 mg of Mg per gram.

Silica--

The data in Table 7 indicate progressive releases of silica over the 93-day period for both the soil and sediment samples under both high-and low-oxygen water conditions. The sediment samples release more silica than found for the soils (about 3 mg of SiO_2 per gram of sediment and 1.8 mg of SiO_2 per gram of soil). Using deionized water as the leaching medium resulted in a 25% increase in dissolved silica.

Projection of Release Values to Lake Superior Chemical Inputs

The magnitudes of the chemical parameter inputs to Lake Superior from shoreline erosion (for those parameters considered thus far) may be estimated from the data presented in Table 5 (seven-week leaching) and Table 8 (3-month leaching). Particle-size distributions for some soil samples are shown in Table 9. For a number of these samples, only the sand-size particle percentages were determined during the wet-sieving process. The data for LS-2, BC-1, BC-3, B-1, N-1 and LS-5 indicate that generally less than 10% of the soil sample consists of sand-size particles. Sample BC-2 was collected at a point 5 feet from Lake Superior and some of the fine material may have been washed out of the soil by wave action before it was collected. Consequently, approximately 90% of the material in the soil samples were used in the seven-week leaching experiments and silica-leaching studies. As stated in the introduction, the total amount of eroded material entering Lake Superior in Wisconsin due to shoreline erosion is estimated at 8×10^6 metric tons. Due to the small percentage of sand contained in the samples and the uncertainty of the shoreline erosion estimate, this figure will be used to estimate chemical inputs.

The results of the estimated inputs of the chemical parameters to Lake Superior is summarized in Table 10. The shoreline erosion contribution was computed by using the value of 8×10^6 metric tons of eroded material per

TABLE 9: PARTICLE-SIZE DISTRIBUTION IN CLAY-CONTAINING SAMPLES

Sample*	% Sand >62.5μ	% Silt 3.9 to 62.5μ	% Coarse Clay 1.1 to 3.9μ	% Fine Clay <1.4μ
LS-2	5	57	35	3
BC-1	6	36	51	7
BC-2	31	31	31	7
BC-3	9	19	64	9
B-1	13			
N-1	6			
LS-1	4			
LS-5	4			
NP-1	0.1			

*Samples are described in Table 1.

year. The values for dissolved solids, alkalinity, and silica are denoted as being lower limits because of the continued increase of these parameters with time. The release of many of the parameters were initially large and then assumed a smaller steady increase with time (dissolved solids, alkalinity, and silica) while others reached steady values or even decreased at longer time periods. The time of suspension of the particulate material in Lake Superior water is not well known but since most of the fine material eventually is deposited in deeper regions of the lake (at which point the release from the clays would be associated with flux from the lake sediments), these seven-week leaching studies (93 days for silica) could be considered as reasonable estimates of contributions by suspended clay particles from shoreline erosion. Another factor to be considered is the possible increased releases per unit weight of suspended material in lower solid-to-water suspension ratios. In addition, leaching in large volumes of water, in which case the value of the parameter does not significantly increase in the water, could result in larger releases for some of the parameters.

The estimated inputs for the Nemadji River were computed by using a value of 2.8×10^5 metric tons of material as an annual suspended solids load. This represents predominately fine-sized material in the river and assumes that 54% of the 5.1×10^5 metric tons is carried into Lake Superior.[3] In terms of the contributions from all Wisconsin streams due to suspended-clay particles, the values in Table 10 would be approximately 35% higher since the Nemadji accounts for 86% of the sediment load from Douglas and Bayfield Counties and the river banks in these counties include 80% of the total stream banks which are classified under very severe or severe erosion. Estimates would assume that particles from the Nemadji River are similar in properties to those from other rivers.

TABLE 10: CHEMICAL RELEASES AND INPUTS TO LAKE SUPERIOR FROM SHORELINE AND RIVER EROSION

Parameter	Chemical Release From Clays (mg parameter per gram of sample) Soils	Chemical Release From Clays (mg parameter per gram of sample) River Particulates	Inputs to Lake Superior From Erosion (metric tons per year) Shoreline Erosion	Inputs to Lake Superior From Erosion (metric tons per year) Nemadji River Particulates
Dissolved Solids*	24 ± 3**	40 ± 5	192,000 ± 40,000	11,000 ± 1,400
Alkalinity* ($CaCO_3$)	23 ± 2	35 ± 5	184,000 ± 40,000	9,800 ± 1,400
Orthophosphate*** (PO_4)	0.030 ± 0.010	0.150 ± 0.050	240 ± 80	43 ± 13
Total Soluble P	0.036 ± 0.020	0.060 ± 0.030	280 ± 160	17 ± 9
Nitrate (NO_3)	0.05 ± 0.05	3 ± 1.5	400 ± 400	840 ± 430
Chloride	< 0.1	-----	< 800	-----
Total Kjeldahl N	< 0.2	< 0.5	< 1,600	< 130
Sodium	0.25 ± 0.20	-----	2,000 ± 1,600	-----
Potassium	0.42 ± 0.15	0.25 ± 0.20	3,400 ± 1,200	69 ± 55
Calcium	6 ± 3	-----	48,000 ± 24,000	-----
Magnesium	0.9 ± 0.4	1.5 ± 1.0	7,200 ± 3,200	430 ± 280
Silica*	1.8 ± 0.4	-----	14,400 ± 3,200	-----

*Lower limits since the values were still increasing at the termination of the experiments.
**The uncertainties are estimated from consideration of standard deviations for the soil samples (Table 5), interlaboratory analytical comparisons, and fluctuations in the analysis of the parameter with time (Appendixes A and B and Table 7).
***See also Section 6.

SECTION 5

WATER-SEDIMENT CHEMICAL PARAMETER EXCHANGE AND SEDIMENT-INTERSTITIAL WATER CHARACTERISTICS

GENERAL PROCEDURES

The chemical characteristics of the interstitial waters in near-shoreline and river sediments containing clay minerals in conjunction with information pertaining to the degree and rate of exchange of chemical components across the sediment-water interface is important in understanding the effects of sediment leaching and sediment resuspension on the chemical composition of the lake waters. Information on sediment leaching and resuspension effects was obtained by collecting core samples thought to be characteristic of red clay-containing river or lake bottom. Chemical analysis was performed on the interstitial water and water overlying the sediment along with certain analysis of the sediment itself. Sediment cores from the same locations as those analyzed at the time of collection were stored at 4°C and the interstitial and overlying water reanalyzed at one month and in some cases two-month periods.

Four sampling locations were chosen for obtaining core samples (Figure 1). Five or six cores at each location were collected in 2-1/2 inch i.d. (6.3 cm) cellulose acetate butyrate core liners which were 4 feet (1.2 m) in length. One set of cores was taken from the bed of the Nemadji River at approximately a 10-foot (3.0 m) depth. This set of cores was obtained by a diver. The clay material in these cores is probably characteristic of the original glacially deposited lacustrine red clay which is being eroded by the river flow. A second set of cores was collected from the near-shoreline region of Lake Superior approximately one mile (1.6 km) west of Bardon Creek in a water depth of one foot (0.3 m). The clay material in these cores also could be representative of originally deposited clay but in addition might contain contributions from clay material which had entered the lake from shoreline erosion upon the collapse of a section of clay bank. The appearance and consistency of the solid material was that of hard-packed red clay with some interdispersal of gray clay. A third sampling location was approximately 1/2 mile (0.8 km) east of the Superior entry to the Superior Harbor (Superior, Wisconsin) at a water depth of 72 to 75 feet (22 to 23 m) at a 3-mile (4.8 km) perpendicular distance from the Lake Superior shoreline. Cores at this location were obtained using a Benthos-type 217 gravity corer. The sediment was loosely packed material characteristic of recently sedimented particulates. The fourth location was approximately 1/2 mile (0.8 km) east of Dutchman's Creek at a water depth of 68 to 72 feet (21 to 22 m) at a

perpendicular distance of approximately four miles (6.4 km) from the Lake Superior shoreline. These sediments also contained recently deposited material.

Attempts to obtain core samples containing significant quantities of deposited clay from shallower regions of the lake were unsuccessful. At these shallower regions, the sediment consisted of sand and gravel although a fine layer of clay covered the fine sand at certain locations. This indicates that the large majority of clay-sized particles entering Lake Superior from erosion are transported to deeper areas of the lake.

The cores consisted of material which occupied from seven to fifteen inches of the core liner with the remainder of the space filled with overlying Lake Superior water. Generally, the smaller clay cores were obtained from the hard-packed material from the Nemadji River and Bardon Creek area sampling location of Lake Superior.

Upon obtaining the cores, the solid material contained in one core from each location was analyzed for Eh, pH, total volatile solids, chemical oxygen demand, total phosphorus, total iron, Kjeldahl nitrogen,and particle-size (pipet-sedimentation method). All analyses except Eh and pH were performed on two sections of the core (upper layer near the sediment-water interface and a lower layer). The specific analytical procedures are summarized in Appendix C. The remaining cores were stored at 4°C in a constant-temperature room (Environmental Research Laboratory, Duluth, Minnesota). Within two days of sampling, the overlying and interstitial water in the sediment was chemically analyzed. This analysis procedure was repeated at a one-month interval for cores from each location and at a two-month period for the Nemadji River and Dutchman's Creek-area cores.

The method for obtaining the overlying and interstitial water was similar to the procedure used by Glass and Poldoski.[7,8] The overlying water was sectioned into four zones above the sediment. For a given section, a sample was siphoned for a dissolved oxygen sample with the remainder siphoned into an acid-washed polypropylene bottle. A small layer in the lower section (approximately one inch) of water was left above the sediment. The core liner was transferred to a nitrogen glove bag and the system flushed with nitrogen. The remaining one inch of water above the sediment was removed by pipet and added to the lowest section of the overlying water. The sediment was then pushed up the liner and 1-1/2-inch sections were sliced and placed in Whirl Pak bags. Generally, three 1-1/2-inch sections were obtained. The sediments in the bags were homogenized and the contents of each were transferred to interstitial water preparation cells.[7] The cells were pressurized with nitrogen (40 psi), centrifuged at 4°C at 2400 rpms (1,580 X g) for 1/2 hour, repressurized twice,and centrifuged for two more 1/2-hour periods. The water preparation cells were returned to the glove bag and the extracted interstitial water was filtered using 0.1 micron membrane filters directly into acid-conditioned polypropylene bottles.

Unfiltered portions of the overlying water were analyzed for pH, specific conductance, dissolved oxygen, and alkalinity while filtered portions (0.45 micron filters) were analyzed for orthophosphate, silica, sodium,

potassium, calcium, magnesium, copper, manganese, cadmium, zinc, iron, aluminum, lead, chromium, and nickel. The interstitial water was analyzed for the same parameters except pH, alkalinity, specific conductance, and dissolved oxygen. In addition, interstitial water from one Dutchman's Creek-area core and one Superior entry-area core was sent to the EPA, Region V Laboratories, Chicago, for mercury, arsenic, and selenium measurements.

Upper and lower-layer sediment samples from a Superior entry-area core were sent to ABC Analytical Biochemistry Laboratories, Columbia, Missouri. These samples were analyzed for chlorinated hydrocarbons, PCBs, arsenic, cadmium, zinc, lead, selenium, and mercury.

RESULTS

The analysis of the core samples for a number of parameters is summarized in Tables 11 and 12. The particle-size analysis shows that the cores composed of glacially deposited material (Nemadji River and Bardon Creek) contained higher percentages of finer-sized particles than the Lake Superior sediment cores (Superior entry and Dutchman's Creek). The percentages designated as A represent the distribution of material into particle sizes if it was dispersed in water while those percentages designated as B were measured using a peptizer (Calgon) and are representative of the actual particle-size distribution in the samples. The Superior entry and Dutchman's Creek cores contained large amounts of fine sand-size particles and only about 10% in the clay-size range. Consequently upon resuspension, only about 10% of the material in the sediment would remain suspended for relatively longer time periods. For example, all particles greater than 3.9 microns settle a distance of about 4 feet (1.2 m) in 24 hours at 20°C in still waters. The Bardon Creek area core contained high percentages of clay-size particles which are the source of much of the continual water turbidity near the Bardon Creek to Amnicon River shoreline area.[7]

The Dutchman's Creek-area Lake Superior core contained a much higher percentage of phosphorus in comparison to the others. The Nemadji River core had the highest percentage of oxygen-demanding material. The Lake Superior sediments contained smaller percentages of iron than those cores representative of the glacially deposited material.

Chemical analysis for chlorinated hydrocarbons and certain metals (by ABC Analytical Biochemistry Laboratories, Columbia, Missouri) on the Superior entry core and one clay soil sample obtained from clay banks along the Nemadji River is tabulated in Table 13. The results for the chlorinated hydrocarbons show that only aldrin was detectable in any of the samples within the limits of measurement. The upper layer of the Superior entry sediment sample was higher than the lower layer in all detectable metals. There were no large differences between the levels of metals in the soil and sediment samples.

The results of the analysis of the interstitial and overlying water in the cores from the four areas are tabulated in Tables 14, 15, 16 and 17. The data from two of these areas have been plotted in Figures 2 and 3.

TABLE 11: SEDIMENT CORE ANALYSIS

Parameter	Depth* (Cm)	pH	Total Solids (%)	COD** (ppm)	Total P** (ppm)	Total Fe** (%)	Kjeldahl N** (ppm)	Eh (mv)
Sample								
Nemadji	3.8		61.5	34,450	18.4	2.7	480	+460 at 0.25 cm
		6.2	± 62.4	± 35,900	± 15.7	± 2.7	± 450	↓
River	8.9		x̄=61.9	x̄=35,150	x̄=17.1	x̄=2.7	x̄= 465	+405 at 4.1 cm
Superior	3.8		66.8	18,650	17.1	1.7	304	+20 at 0.64 cm
		6.6	± 74.2	± 7,050	± 24.2	± 2.1	± 540	↓
Entry	8.0		x̄=70.5	x̄=12,850	x̄=20.7	x̄=1.9	x̄=422	-161 at 4.4 cm
Bardon	2.2		58.8	10,650	2.3	4.8	210	+55 at 0.63 cm
		7.0	± 63.8	± 6,750	± 5.2	± 5.1	± 208	↓
Creek	7.9		x̄=61.3	x̄=8,700	x̄=3.8	x̄=5.0	x̄=209	+60 at 3.8 cm
Dutchman	1.6		70.4	10,300	65.8	1.6	220	+136 at 0.64 cm
		6.3	± 67.3	± 7,700	± 45.7	± 2.4	± 165	↓
Creek	7.3		x̄=68.9	x̄=9,000	x̄=55.8	x̄=2.0	x̄=193	+173 at 3.8 cm

*Value given is midpoint of depth of core sample analyzed from top. Complete sample includes between 1.3 to 2.5 cm on either side of depth value.
**Value based on sample dried at 105°C.

TABLE 12: PARTICLE-SIZE ANALYSIS

Parameter		% Sand (>62.5μ)		% Silt (3.9-62.5μ)		% Coarse Clay (1.4-3.9μ)		% Fine Clay (<1.4μ)	
Sample	Depth (Cm)	A*	B*	A*	B*	A*	B*	A*	B*
Nemadji	3.8	9	9	74	65	6	9	11	17
River	8.9	10	9	71	76	8	4	11	11
Superior	3.8	74	65	15	19	9	4	2	12
Entry	8.0	79	82	8	7	7	9	4	2
Bardon	2.2	6	9	50	14	20	39	24	38
Creek	7.9	14	9	31	11	18	11	38	69
Dutchman	1.6	81	68	12	9	6	9	1	13
Creek	7.3	71		15		8		6	

*A refers to sample dispersed in distilled water and B refers to sample dispersed in distilled water with peptizer added.

TABLE 13: CHEMICAL ANALYSIS* OF SUPERIOR ENTRY LAKE SUPERIOR CORE AND NEMADJI RIVER SOIL SAMPLE

Sample**	PCB	Aldrin	p,p'-DEE, Dieldrin	Endrin, o,p-DDT, p,p'-DDE, p,p'-DDT	Pb	Hg	Zn	Se	As	Cd
Superior Entry, Upper Layer of Sediment	<0.04	<0.002	<0.004	<0.01	8.6	0.113	31.9	<0.01	12.2	0.23
Superior Entry, Lower Layer of Sediment	<0.04	<0.002	<0.004	<0.01	3.2	0.104	22.1	<0.01	9.0	0.03
Nemadji River Soil Sample	<0.04	0.003	<0.004	<0.01	7.2	0.202	38.2	<0.01	11.1	0.16

*All values are in parts per million on a wet sample basis. The concentrations of α-BHC, lindane, heptachlor, heptachlor epoxide, α and β-chlordane were less than 0.002 ppm for all samples.
**Samples contained 46.8, 30.3 and 30.2% water, respectively.

TABLE 14: CHEMICAL ANALYSES OF NEMADJI RIVER SEDIMENT CORE AND OVERLYING WATER

Distance From Sediment-Water Interface (cm)		pH	S.C.*	O_2 mg/l	PO_4 µg PO_4/l	Alk**	SiO_2 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cu µg/l	Mn µg/l	Cd µg/l	Zn µg/l	Fe µg/l	Al µg/l	Pb µg/l
62	75-100	7.35	272	8.1	11	134	11.6	4.7	1.32	42.3	10.1	4.6	2.8	0.15	3.4	166	36	<0.1
	50-75	7.40	272	8.4	9	131	11.1	4.9	1.41	39.0	10.3	5.0	3.1	0.14	3.3	231	28	<0.1
	25-50	7.41	272		12	131	11.6	4.9	1.39	39.3	10.1	5.2	3.9	<0.1	4.0	171	33	0.2
	0-25	7.42	272	8.1	32	134	11.4	5.3	1.33	38.1	9.9	6.0	10.1	<0.1	1.9	102	25	0.3
Day	0						Sediment-Water Interface											
	0-3.8				154		15.9	6.3	1.91	51.0	12.1	5.8	1590	0.4	42	82	12	0.7
	3.8-7.6				835			10.5	1.99	72.0	12.4	24.2	820	0.7	57	35	274	6.1
Values	7.6-11.4																	
30	75-100	7.50	255	5.9	10	118	10.6	3.8	1.16	33	8.5	3	8.0	<0.1	5.8	260	92	2.0
	50-75	7.51	255	5.8	2	118	10.6	3.7	1.14	33	8.5	3	6.2	<0.1	4.4	240	90	1.5
	25-50	7.51	255	6.0	12	121	10.7	3.7	1.16	34	8.5	4	10.2	<0.1	5.2	260		1.5
	0-25	7.82	267	6.9	12	153	11.2	4.5	1.08	38	13.0	2	90	<0.1	2.5	66	42	0.5
Day	0						Sediment-Water Interface											
	0-3.8						18.3	6.1	1.89	37.8	11.9	8	1000	0.2	13.4	210	42	2.5
	3.8-7.6						15.2					40	380	3.5	83	100	200	3.2
Values	7.6-11.4																	
	50-100			8.7	35		10.1	4.2	1.25	34.6	9.5	10	24.0	0.1	13.0	200		<1
Initial	0-50			7.6	38		10.3	4.1	1.31	29.8	9.7	5	22.7	0.1	5.8	193		<1
	0						Sediment-Water Interface											
	0-3.8	6.2			138		19.6	6.5	1.80	32	10.8	10	2000	1.0	26			13.3
Values	3.8-7.6				236		23.1	6.7	1.80	32	10.5	15	3000	1.0	35			15.2
	7.6-11.4				471		26.8	>10	1.80	35	11.8	20	5000	1.0	35			24.4

*Specific Conductance in micromhos/cm.
**Alkalinity in mg of $CaCO_3$ per liter.

TABLE 15: CHEMICAL ANALYSES OF SUPERIOR ENTRY AREA CORE AND OVERLYING WATER

	Distance From Sediment-Water Interface (cm)	pH	S.C.*	O_2 mg/l	PO_4 µg PO_4/l	Alk**	SiO_2 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cu µg/l	Mn µg/l	Cd µg/l	Zn µg/l	Fe µg/l	Al µg/l	Pb µg/l
31	75-100	7.07	108	7.7	6	52.3	3.32	1.9	0.60	16.5	3.5	3.3	1.3	0.2	5.2	26	11	<0.1
	50-75	7.09	107	8.7	10	53.2	3.97	1.7	0.64	16.2	3.4	2.7	4.6	0.4	4.5	16	6	0.2
	25-50	7.08	108	7.5	14	53.3	2.95	1.6	0.63	16.7	3.4	1.3	1.6	<0.1	4.1	16	8	0.2
	0-25	7.03	108	7.3	12	53.8	4.60	1.6	0.62	15.9	3.4	2.1	1.1	<0.1	4.0	17	6	0.2
Day	0							Sediment-Water Interface										
	0-3.8				78		8.9	2.4	2.7	27	7.0	4.9	520	0.1		35	22	<0.1
	3.8-7.6				53		13.4	2.4	2.6	22	6.6	4.0	680	0.2		50	14	0.2
Values	7.6-11.4				249			2.4	2.5	22	6.0	4.9	620	0.1		44	31	1.0
	0-100	7.32	98	11.7	3	43.9	3.1	1.9	0.50	13.8	3.3	1.5	1.7	<0.1	4.6	45	46	<0.5
Initial	0							Sediment-Water Interface										
	0-3.8	6.60			12		18.8	4.6	2.5	33	9.7	5	1070	1.6	7	190	134	8.3
Values	3.8-7.6				20		21.0	4.0	3.0	41	12.1	14	1600	3.3	22	210		16
	7.6-11.4				24		14.7	5.8	2.1	26	9.2	26	470	4.8	32		29	28

*Specific Conductance in micromho's/cm.
**Alkalinity in mg of $CaCO_3$ per liter.

TABLE 16: CHEMICAL ANALYSES OF BARDON CREEK-AREA CORE AND OVERLYING WATER

Distance From Sediment-Water Interface (cm)		pH	S.C.*	O_2 mg/l	PO_4 µg PO_4/l	Alk**	SiO_2 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cu µg/l	Mn µg/l	Cd µg/l	Zn µg/l	Fe µg/l	Al µg/l	Pb µg/l
30	75-100	7.30	121	8.2	9	56.0	3.19	3.1	0.80	15.5	3.7	3.5	3.0	<0.1	2.6	66	53	0.7
	50-75	7.29	121	8.6	9	54.6	3.36	3.2	0.79	16.3	3.7	3.5	2.3	<0.1	2.6	42	36	0.5
	25-50	7.30	121	7.4	10	57.5	3.32	3.2	0.79	16.0	3.7	2.7	8.3	<0.1	1.5	60	45	0.3
	0-25	7.30	122	7.9	16	56.8	3.39	3.2	0.80	16.8	3.8	3.5	4.1	<0.1	1.6	54	36	1.4
Day	0						Sediment-Water Interface											
	0-3.8				181		<4.5	11	1.6	37	11.5	43	115	1.3	4	42	56	0.2
	3.8-7.6											13	110	4.3	55	75	21	1.0
Values	7.6-11.4																	
	0-100	7.99	107	8.8	10	51.5	3.07	1.9	0.77	15.3	3.7	3.5	13	0.3	7.6	91	142	0.7
Initial	0						Sediment-Water Interface											
	0-3.8	6.9										31	1250	1.1	13.3	234	166	4.0
Values	3.8-7.6											15		1.0	12.7	175	160	5.0
	7.6-11.4																	

*Specific Conductance in micromho's/cm.
**Alkalinity in mg of $CaCO_3$ per liter.

TABLE 17: CHEMICAL ANALYSES OF DUTCHMAN'S CREEK-AREA CORE AND OVERLYING WATERS

Distance From Sediment-Water Interface (cm)		pH	S.C.*	O_2 mg/l	PO_4 µg PO_4/l	Alk**	SiO_2 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cu µg/l	Mn µg/l	Cd µg/l	Zn µg/l	Fe µg/l	Al µg/l	Pb µg/l
60	75-100	6.94	108	7.1	3	56		1.64	0.62	15.6	3.64	1.9	5.8	0.1		31		<0.1
	50-75	6.93	108	6.6	2	55		1.69	0.64	15.8	3.68	1.3	6.4	<0.1		20		0.6
	25-50	6.91	111	6.6	2	55		1.70	0.61	15.3	3.74	3.3	99.2	0.2		18		<0.1
	0-25	6.88	116	6.4	23	56		1.72	0.60	16.4	3.69	2.5	534	0.1		49		0.6
Day	0	Sediment-Water Interface																
	0-3.8				36			3.5	1.7	37	13	3.2	4100	0.4		2800		1.6
	3.8-7.6				57			3.4	1.8	44	16		7800			6200		<0.1
Values	7.6-11.4				1770			3.5	1.7	47	16	1.6	7800	0.6		12600		<0.1
31	75-100	7.04	106	7.9	3	49.6	3.41	1.68	0.63	16.2	3.9	2.5	3.0	0.1	7.4	13	5	<0.1
	50-75	7.09	106	7.7	2	52.7	3.56	1.84	0.60	16.3	3.9	2.3	2.1	0.1	5.9	8	7	<0.1
	25-50	7.10	106	7.9	1	51.6	3.42	1.64	0.61	15.8	3.8	2.3	3.0	<0.1	5.4	14	21	<0.1
	0-25	7.09	107	7.8	6	53.8	3.52	1.64	0.63	14.9	3.8	3.5	5.8	<0.1	5.0	10	12	0.7
Day	0	Sediment-Water Interface																
	0-3.8				70		<9	3.4	1.8	36	15	9.2	3700	0.2	15.5	1550	81	2.3
	3.8-7.6				36		19	3.6	1.9	40	12	1.9	3800	<0.1	2.6	4770	15	0.3
Values	7.6-11.4				44		33	3.4	1.6	28	9.3	3.2	2800	<0.1	1.4	3950	16	1.0
Initial	0-100	7.3	98	11.4	14	44.6	3.15	1.88	0.53	13.9	3.3	2.5	3.4	<0.1	4.9	32	60	0.5
	0	Sediment-Water Interface																
	0-3.8	6.3			5		19.5	3.4	1.7	20	6.6	3	720	0.5	9.4	94	77	6.0
	3.8-7.6				40		33.9	5.2	1.8	25	7.7	3	1400	0.5	9.4			2.0
Values	7.6-11.4				435		41.0	3.9	1.3	21	6.6	3	1100	0.3	2.5	227	31	3.0

*Specific Conductance in micromho's/cm.
**Alkalinity in mg of $CaCO_3$ per liter.

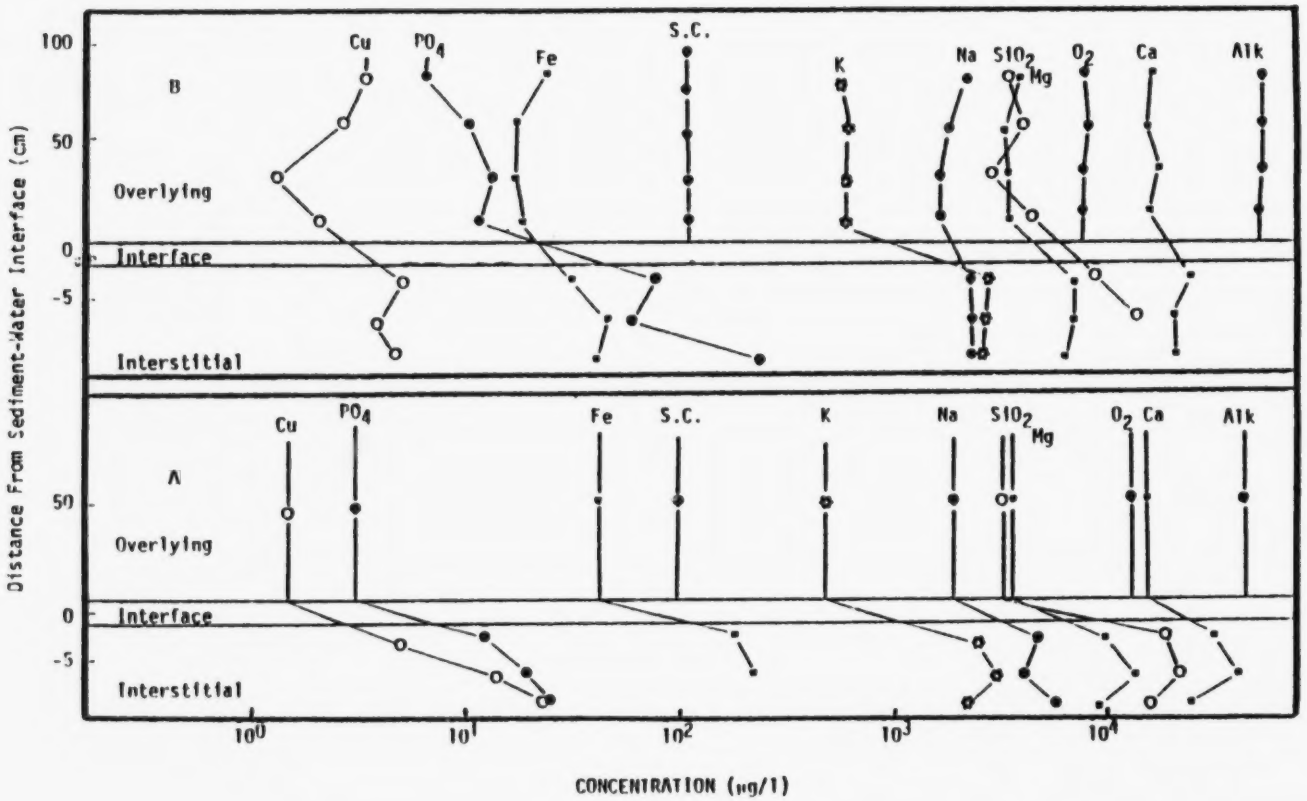

Figure 2. Comparison of the chemistry of overlying and interstitial waters for the Superior entry-area core after initial removal from Lake Superior (A) and after storage for 31 days at 4°C (B).

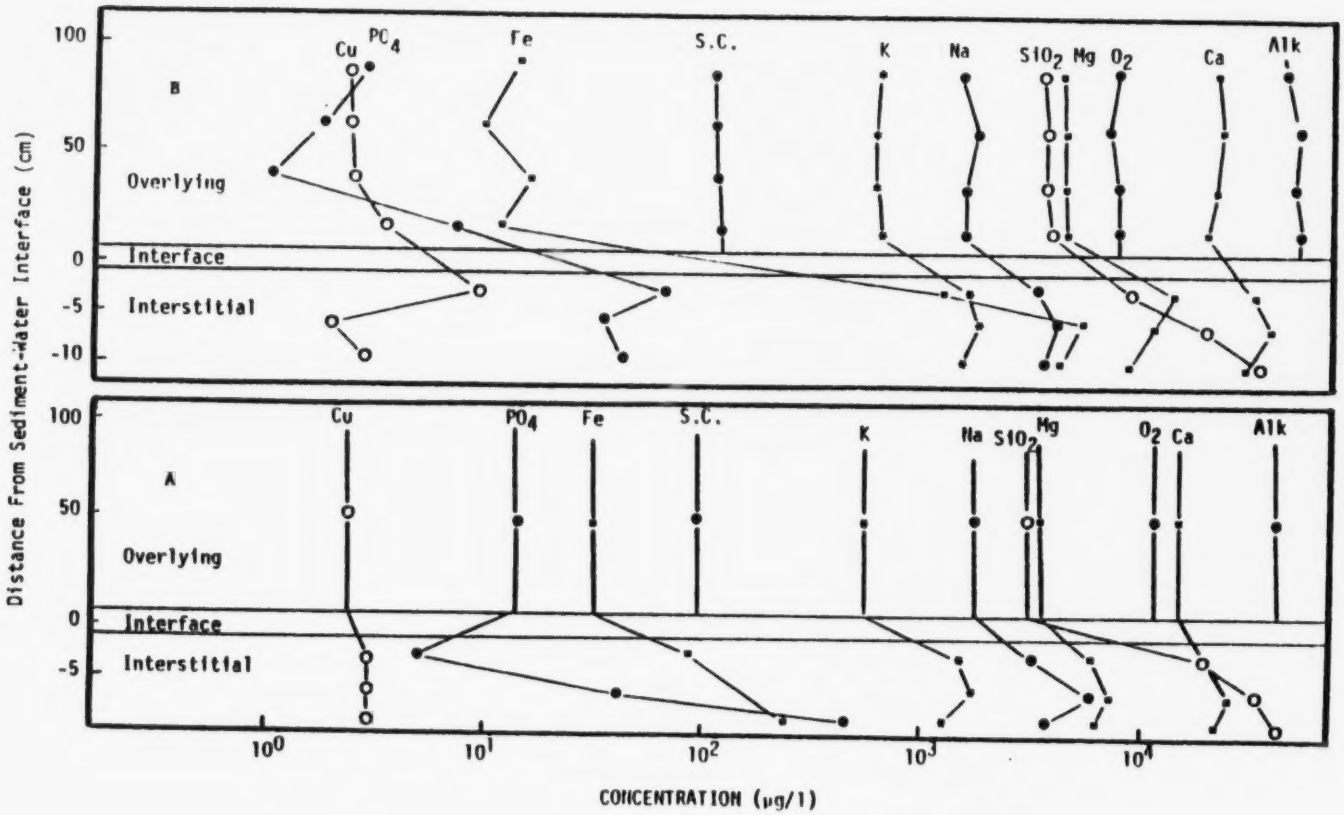

Figure 3. Comparison of the chemistry of overlying and interstitial waters for the Dutchman's Creek-area core after initial removal from Lake Superior (A) and storage for 31 days at 4°C (B).

The interstitial waters of the sediments are generally enriched in orthophosphate, silica, sodium, potassium, calcium, magnesium, copper, manganese, cadmium, zinc, iron, aluminum, and lead compared to the values for the overlying water. Parameters in the overlying water which showed an increase with time are specific conductance (dissolved solids), silica, potassium, calcium, magnesium, and alkalinity. In some cases, sodium and orthophosphate also increased in the overlying water with time. Most of the heavy metals appeared to decrease with time in the overlying water which may reflect adsorption on the container walls or adsorption to particulates in the water present at the time of collection which subsequently settled to the sediment.

CHEMICAL INPUTS FROM INTERSTITIAL WATER OF RESUSPENDED SEDIMENTS

It is difficult to assess the chemical inputs to Lake Superior from resuspension of sediments with the information currently available. One would need to know the rate of chemical enrichment of the interstitial waters of the sediments for the various parameters, the total amount of sediment resuspended on a yearly basis, and the average time that the particulate matter remains settled before being resuspended. It would be of interest to determine the concentrations of the chemical parameters in the interstitial water in the sediments just prior to spring breakup of ice cover since a particularly heavy load of nutrients and trace metals would be expected to be released upon disturbing the sediments at this time. The rates of enrichment of the sediments might be estimated from laboratory studies on cores in which layers of clay particles are allowed to settle on the surface of the sediment in the cores and these surface layers analyzed as a function of time.

From the data currently available, a gross estimate of chemical releases due to resuspension can be made. Sydor[3] has reported an estimate of the amount of fine particulate matter resuspended per year as 1.6×10^6 metric tons. The portion of the lake bottom resuspended is mainly located in a 10-to-25 mi^2 (26-to-65 km^2) area of the southwestern end of the lake. Since much of this is resuspended more than once, a value of 5×10^5 metric tons is the approximate amount of fines which is subjected to resuspension. Considering the sediments from the upper layers of the Superior entry and Dutchman's Creek areas, the data show an average water content of 39%. Limited observations on the water content of the upper 0.5 to 1.0 cm of sediment indicate a water content of about 60%. Consequently, 3.0×10^5 metric tons of interstitial water would be associated with 5×10^5 metric tons of these upper-layer sediments. Considering the probability that some sediment material whose particle size is larger than the clay-size particles (fines) will be distributed under certain turbulence events, the amount of interstitial water associated with resuspension should be somewhat greater than the value estimated from considering the fines alone. Consequently, a rough estimate of the amount of interstitial water associated with resuspension is 5×10^5 metric tons.

Using the average values of the chemical parameters for the interstitial waters of the upper layers of the Superior Entry and Dutchman's Creek sediments and the value of 5×10^5 metric tons of interstitial water

dispersed in the lake per year, the estimates of inputs of each parameter are given in Table 18. These inputs are generally quite small compared to inputs from other sources. The inputs for orthophosphate, silica, sodium, potassium, calcium, and magnesium are insignificant compared to those values for shoreline and river erosion of soils given in Table 10. Input values for the heavy metals and aluminum are also small. Increasing these inputs by a factor of ten would still result in relatively small values. However, additional releases of certain of the parameters due to leaching of the resuspended particles would occur. The input values for certain of the heavy metals and aluminum will be considered further in Section 7 when leaching studies of soils is considered for these parameters.

TABLE 18: ESTIMATES OF CHEMICAL INPUTS IN LAKE SUPERIOR DUE TO INTERSTITIAL WATERS OF RESUSPENDED SEDIMENT

Chemical Parameter	Average Value For Interstitial Water (mg/l)	Inputs From Resuspension (metric tons per year)
Orthophosphate (PO_4)	0.009	0.0045
Silica (SiO_2)	19.1	9.5
Sodium	4.0	2.0
Potassium	2.1	1.0
Calcium	26	13
Magnesium	7.1	3.6
Manganese	0.90	0.45
Cadmium	0.001	0.0005
Zinc	0.008	0.004
Iron	0.092	0.045
Aluminum	0.105	0.05
Lead	0.007	0.004
Copper	0.004	0.002

SECTION 6

SORPTIVE CHARACTERISTICS OF CLAYS

GENERAL PROCEDURES

The ability of clay-laden soil or sediment samples to control the aqueous concentrations of certain chemical species through primarily sorptive processes was investigated. These studies involve the preparation of clay-solution suspensions containing a range of concentrations of the particular chemical parameter under investigation resulting in various chemical parameter-clay ratios. After predetermined equilibration times, the aqueous phase is analyzed for the chemical parameter and the magnitude of concentration changes due to interactions of the chemical species with the clays is calculated. These concentration changes with respect to the weights of the clays in the suspensions are used to calculate sorption isotherms.

The chemical parameters investigated include orthophosphate, phenols, and certain trace metals. A summary of the experimental methods, conditions, and results are enumerated below:

ORTHOPHOSPHATE STUDIES

Experimental Procedure

Standard orthophosphate solutions in the range of 0.05 to 0.5 mg/l were prepared from dilutions of a 500 mg/l solution of $CaH_4(PO_4)_2$. Weighed quantities of the clay sample were added to the standard orthophosphate solutions in duplicate to prepare desired suspended-solid concentrations. The suspensions were agitated by shaking the Pyrex containers periodically over a two-hour period.

It had been previously determined that a two-hour period was sufficient to complete at least 90% of the phosphate exchange with the clays. Lake Superior water obtained from the lake intake at the Environmental Research Laboratory, Duluth, Minnesota was used in preparing the solutions.

After the two-hour equilibration time, the suspensions were filtered through 0.45μ membrane filters and the aqueous phase analyzed for orthophosphate concentrations. Controls containing Lake Superior water spiked with orthophosphate were run to determine possible losses or gains during glassware contact and filtration. The controls indicated no loss or gain of orthophosphate due to these effects.

The clay soil samples used in this study had been air-dried at room temperature. The remaining moisture content was determined by heating sub-samples at 120°C for two hours. The clay sample was ground in a mortar and pestle and sieved through a 120-mesh sieve to remove coarse particles in the sand-size range.

The sediment sample used was the Lake Superior Dutchman's Creek top-layer sediment. It was the same sample from which the interstitial water had been previously removed for analysis in the core-leaching experiments. The sediment was weighed in the moist state under a nitrogen atmosphere in a dry box during suspension preparation. Dry weights for the sediment samples were measured in the same manner as described for the soil samples.

Treatment of Data

The change in orthophosphate concentration (ΔPO_4) for the aqueous phase is calculated in mg per liter by subtracting the average final phosphate concentration (for duplicate samples) following equilibration with the clay from the initial phosphate concentration of the solution. Changes in phosphate concentration with respect to the clay (mg PO_4 sorbed per kg of clay) are computed using the relationship:

$$\Delta PO_4 \text{ clay} = \frac{-(\Delta PO_4 \text{ solution}) \text{ (V) (lg) } (10^6)}{\text{(W) (1000 mg)}}$$

where ΔPO_4 = change in phosphate concentration in mg/l

V = volume of solution in liters

W = mass of clay in grams

Consequently, negative ΔPO_4 clay values represent a net desorption from the clay and positive values correspond to a net adsorption by the clay.

A plot of ΔPO_4 clay versus the final concentration of orthophosphate in the solution establishes a sorption isotherm for the particular clay sample. The slope or slopes of the isotherm is a measure of the buffering capacity of the clay sample toward orthophosphate. The concentration of orthophosphate at which ΔPO_4 clay equals zero is referred to as the equilibrium phosphate concentration (EPC) for the clay sample and denotes the concentration of phosphate in the water at which no net phosphate exchange will occur upon addition of the clay sample to the solution.[9]

Results and Discussion

Nine soil samples were studied for their phosphate exchange capacities toward orthophosphate. These soil samples have been described in Table 1. The suspensions used in this investigation contained a soil-to-solution ratio of 1000 mg/l. The temperature for the study was 23 to 25°C. A graphical presentation of the results is given in Figure 4.

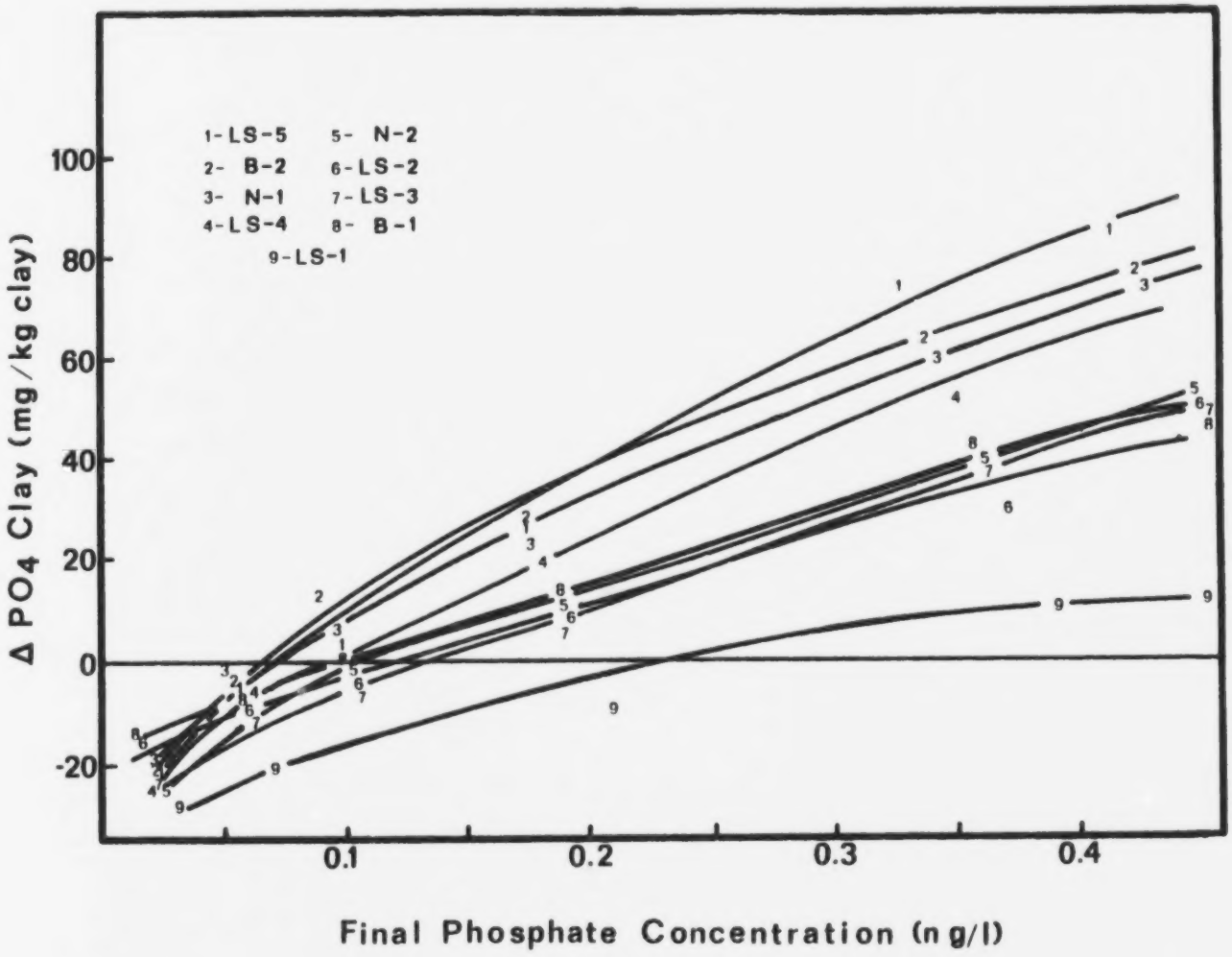

Figure 4. Sorption isotherms for soil samples.

An investigation of one soil sample at various soil suspensions ranging from 10,000 to 300 mg/l showed variations in the slopes and EPC values with the result that the EPC values increase along with an increase in the slope of the isotherm as the soil-to-solution ratio decreases. Consequently, the data in Figure 4 would only approximate sorption behavior under conditions when the concentrations of particles in Lake Superior water are lower than 1000 mg/l.

The EPC values lie in the range of 0.06 to 0.21 mg/l for the samples. The gray clay sample (LS-1) has the largest EPC value along with the lowest slope for the isotherm. Since the concentration of orthophosphate in Lake Superior water is well below these EPC values (about 0.005 mg/l or less), there would be a net input of orthophosphate into Lake Superior upon erosion of these soils. At a final orthophosphate solution concentration of 0.005 (approximating Lake Superior), the ΔPO_4 values range from about -18 to -30. Considering the -30 value, an amount of 30 tons of orthophosphate would be released to Lake Superior waters per megaton of eroded material. Using the previously listed value of 8×10^6 metric tons per year of shoreline-eroded soil material, an estimate of the annual orthophosphate input to Lake Superior can be made.

$$PO_4 \text{ input} = (8 \times 10^6 \text{ tons soil}) \left(\frac{30 \text{ tons } PO_4}{10^6 \text{ tons soil}} \right) = 240 \text{ tons}$$

Since the fine material will attain low soil-to-solution ratios upon its erosion and dispersal in the lake water and our studies indicate a larger negative value of ΔPO_4 under lower soil-to-solution ratio conditions, the PO_4 input value listed above would only be a lower limit to the actual input. However, obtaining isotherms at low soil-to-solution ratios is difficult since small errors in the determination of orthophosphate concentrations in the solutions result in relatively large errors in the ΔPO_4 values, compared to higher soil-to-solution ratios. In addition, the clay particles do exhibit a buffering effect in that uptake of orthophosphate by organisms in the water (thereby lowering its concentration) could result in a further release of orthophosphate to the waters. It is also possible that some organisms may directly remove orthophosphate upon contact with the clay particles. In view of these factors, we could not estimate the upper limit to the orthophosphate input to the water and organisms due to shoreline erosion.

In comparison to the 240 metric tons of PO_4 from shoreline erosion, Plumb and Lee have estimated an influx of about 1800 metric tons of orthophosphate into the western arm of Lake Superior mainly from the Duluth-Superior Harbor.[10]

Erosion of clay material into the rivers can result in a release or uptake of orthophosphate depending upon the concentration already in the water. For example, the data for samples N-1 and N-2 indicate that Nemadji River water containing orthophosphate levels above the 0.07 to 0.10 ppm range will exhibit a reduction in orthophosphate whereas the opposite is true for waters containing lower orthophosphate values. The eroded material would

result in a net input of orthophosphate into the river water during lower flow periods but probably remove orthophosphate following extensive land drainage and possible sewage overflows following storm activity. An uptake of orthophosphate by the clay particles will increase their EPC values, and if these particles enter Lake Superior, a larger release of orthophosphate would result than if the particles had not been subjected to river water exposure under higher orthophosphate concentration conditions. This has been shown by the higher orthophosphate release of the Nemadji particulate sample (Section 4).

In order to determine if any large differences in exchange characteristics occur with temperature, one soil sample was investigated at both room temperature and 4°C. The latter temperature would be characteristic of Lake Superior shoreline area waters at certain times of the year. The result showed little difference in the EPC value of the sorption isotherm (0.090 at 4°C and 0.088 at 23°C). Some decrease (~30%) in the slope occurred in the higher final orthophosphate concentration region of the isotherm, although in the low final orthophosphate region the isotherms were very close. Thus the conclusions stated above are unchanged. This study does indicate that the clay material will remove less orthophosphate from waters containing high levels of the nutrient at lower water temperatures.

The results of the investigation of the upper layer of the Lake Superior Dutchman's Creek area sediment is summarized by the data shown in Figure 5. The EPC value of 0.05 indicates that there will be a net input of orthophosphate from the sediment into Lake Superior. Upon resuspension of the material into the lake water, about 32 tons of orthophosphate would be released per megaton of sediment. Using the value of 1.5×10^6 metric tons per year as the amount of clay-sized material resuspended, an estimate of about 50 tons of orthophosphate is released per year due to currents and wave action, causing resuspension in the shoreline regions of the lake. This estimate is based on only one sample, which is assumed to be characteristic of the material resuspended and consequently only a rough estimate. However, the magnitude of the value should be correct. As discussed earlier for soils, smaller clay-to-solution ratios than used in this experiment and uptake of orthophosphate by organisms could increase the orthophosphate contribution from the sediment.

The previously discussed undisturbed core-leaching experiments (Section 5) indicate only a very small contribution of orthophosphate from the interstitial waters of the lake sediments.

METAL LEACHING AND EXCHANGE

Experimental Procedure

Leaching and exchange studies involving certain metals in clay-water systems were carried out using plastic containers, shorter suspension equilibration times, and, in some cases, a higher solid-to-solution ratio than that employed in the seven-week leaching studies described in Section 1. The

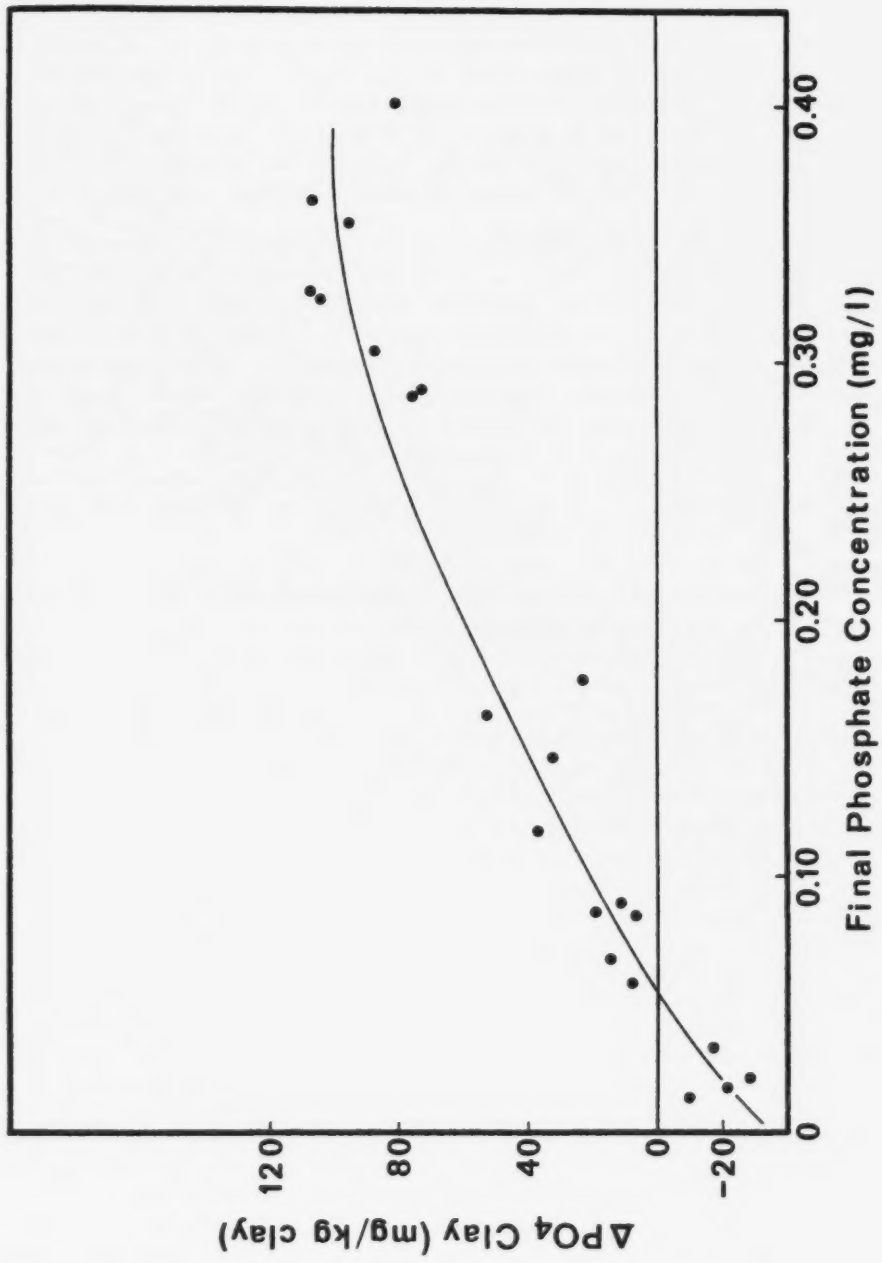

Figure 5. Sorption isotherm for sediment.

shorter equilibration times were chosen in order to minimize losses of the metals on the container surfaces.

One phase of these studies involved leaching of a soil sample (LS-5) as a function of time for a 24-hour period. Approximately one gram samples of the soil were dispersed into 500 ml of Lake Superior water in acid-presoaked bottles. The suspensions were shaken for a fixed time using a laboratory shaker. The suspensions were filtered through either 0.1 or 0.45-micron membrane filters and acidified with HNO_3 until analysis. The clay-solution contact times ranged from a few minutes to 24 hours. All metal analyses were performed by flameless atomic-absorption spectroscopy.

A second phase consisted of leaching some of the sediment samples used in the core-leaching experiments (Section 5) and the LS-5 soil sample for two hours. The same basic procedure was used except that the suspensions containing sediments were prepared under nitrogen to avoid chemical changes due to air exposure. Oxygenated Lake Superior water was used to prepare the suspensions. The sediment samples employed were the upper layer of the Superior entry-area sediment and the upper and lower layers of the Dutchman's Creek-area sediment. These were the same sediments from which the interstitial water was removed for analysis (Section 5). Some of these leachates were sent to the EPA Region V Laboratories, Chicago, for mercury, arsenic, and selenium analysis.

Data has also been obtained on a project under the Sea Grant Program, University of Wisconsin, involving an investigation of the ability of the suspended clay particles to remove metals from aqueous solution. Some of the results will be listed here, as they complement the information obtained in this project. These studies are focused on clay-water suspensions in which various amounts of a particular metal have been added. The suspensions are analyzed after a fixed time for the concentrations of metals remaining in the solution. Sorption isotherms for the clay-metal interactions in the aqueous systems are prepared from this data. The agitated suspensions containing approximately one gram of the LS-5 soil sample per 500 ml of Lake Superior water were analyzed after three minutes, half hour, one hour, two hours, six hours, twenty hours and twenty-four hours of soil solution contact. The results indicated that certain of the metals were being adsorbed on the walls of the polypropylene containers or being readsorbed by the particulates over this time period (particularly aluminum, iron, and lead). As the metals seemed to reach maximum concentrations in the solution within two hours, this time of soil-solution equilibrium was used in leaching studies involving the LS-5 soil sample and the sediment samples.

The exchange of certain of the metals with clay soil particles in aqueous suspensions in experiments in which the suspensions were spiked with varying amounts of the particular metal gives further information on the sorption of the metals. Soil suspensions containing Lake Superior filtered water were prepared in polypropylene bottles and the appropriate metal was added by pipetting sufficient volumes of concentrated standard into the suspension. The initial concentrations of the metals in the spiked suspensions ranged from 10 to 200 µg/l. A duplicate was prepared for each suspension. In addition, two bottles contained suspensions which were not spiked

with the metal and two bottles containing only Lake Superior water and 200 µg/l of the metal were prepared. The latter two bottles were used to check on metal losses due to container adsorption or filtering. All bottles were agitated for one hour in a shaker water bath at 23°C, after which the suspensions were allowed to settle for five minutes. Each sample was filtered using 0.45-micron membrane filters, and the filtrate immediately acidified to 0.05% in HNO_3 until analysis. The filtrates were then analyzed by flameless atomic absorption in order to determine metal exchanges with the suspended clays.

Results and Discussion

The increase in concentrations of the various metals in the leachates compared to the values in lake water are shown in Table 19. The largest increases are found for manganese, aluminum, and iron. The lower layer of the Dutchman's Creek-area sediment released the largest amounts of the metals except for copper. The capacity of the sediments to remove metals from aqueous solutions containing higher concentrations of the metals is shown by the system which was spiked with 200 µg/l each of copper, zinc, cadmium, lead and manganese. All of these metals except iron were reduced to low levels upon interaction with the suspended sediment.

From the data for the LS-5 soil sample and the value of 8×10^6 metric tons of shoreline material eroded annually, estimates of the inputs of metals to Lake Superior were computed and are tabulated in Table 20. Assuming a total of 1.6×10^6 metric tons of resuspended sediment annually, estimates of the metal releases due to this process are also listed in Table 20. The sediment resuspension inputs are based on the average releases for the upper layers of the Superior entry and Dutchman's Creek-area sediments. Since the increases in concentrations of many of the metals after the two-hour clay-water equilibration times were very small to undetectable, only releases of manganese, iron, and aluminum could be determined with some certainty. However, upper limits of metal releases for other metals could be estimated. If the resuspension contribution to metal inputs were ten times higher than listed in Table 20, they would still be less than those due to soil erosion. The resuspension contribution from dispersion of the sediments is much larger than that estimated from the content of the interstitial waters (Section 5) and consequently desorption or solubilization of metals from the suspended particles would be the major mechanisms for the metal inputs.

Figures 6 and 7 show results of the exchange studies for copper and manganese. The gain or release of the metal as a function of the concentration of the metal in the aqueous system is plotted versus the final concentration of metal in the aqueous solution. The "delta metal" values give the mg of metal exchanged with the soil-per-kilogram of the soil. The data shown for copper pertain to 1000 ppm soil suspensions while that for manganese refers to 10,000 ppm suspensions. The "delta metal" values are computed in a similar manner to those for orthophosphate, which is discussed earlier in this section. Negative values of "delta metal" refer to release of the metal from the clay, whereas positive values refer to adsorption of the metal from the solution.

TABLE 19: METAL LEACHING OF CLAY SAMPLES

Sample	Cu	Mn	Cd	Zn	Pb	Cr	Ni	Al	Fe	Hg	As	Se
Lake Water[1]	1.9	0.2	0.01	1.0	<1	<0.1	<10	5	8	<0.1	<2	<5
LS-5 Soil	2.9	5.9	0.01	<10	<1	<0.1	<10	94	81	<0.1	<2	<5
Superior Entry Sediment (upper layer)	1.9	2.3	<.05	4	1	--	<10	49	38	<0.1	<2	<5
Dutchman's Creek Sediment (upper layer)	6.1	3.6	<.05	5	2	--	<10	62	125	--	--	--
Dutchman's Creek Sediment (lower layer)	0.2	310	<.05	9	7	--	--	115	520	--	--	--
Dutchman's Creek Sediment (upper layer)[2]	4.1	5.9	2.5	12	2	--	--	--	148	--	--	--

[1]Concentration of metals in the Lake Superior water used in the leaching experiments. The other values in the table represent increases in concentration over that in lake water. All metal concentrations in µg/l.

[2]Lake Superior water was spiked with 200 µg/l each of copper, zinc, cadmium, lead, and manganese.

TABLE 20: METAL INPUTS FROM SHORELINE EROSION AND SEDIMENT RESUSPENSION

	Shoreline* Erosion (metric tons per year)	Sediment Resuspension (metric tons per year)
Copper	<2.0	<1.0
Manganese	56**	0.4
Cadmium	<0.008	<0.01
Zinc	<8	<0.6
Lead	<1	<0.2
Chromium	<0.1	----
Nickel	<8	<1.5
Aluminum	76 $\pm$ 50	<7.5
Iron	64 $\pm$ 10	<11
Mercury	<0.08	<0.01
Arsenic	<2	<0.25
Selenium	<4	<0.7

*Uncertainties estimated from EPA-UWS Analytical Quality Control Program (Appendix B).
**Determined from exchange studies.

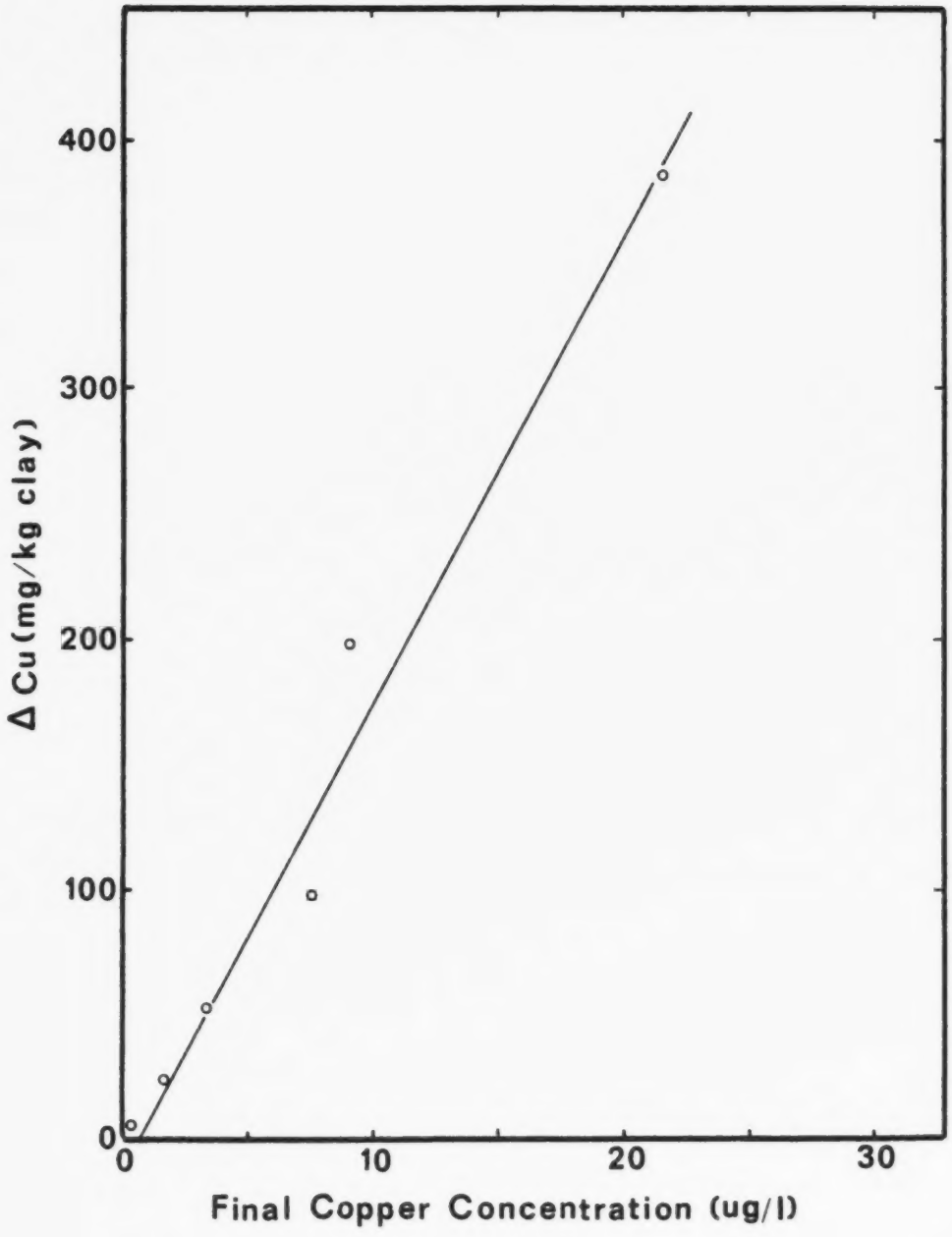

Figure 6. Copper sorption isotherm for clay soil in Lake Superior water.

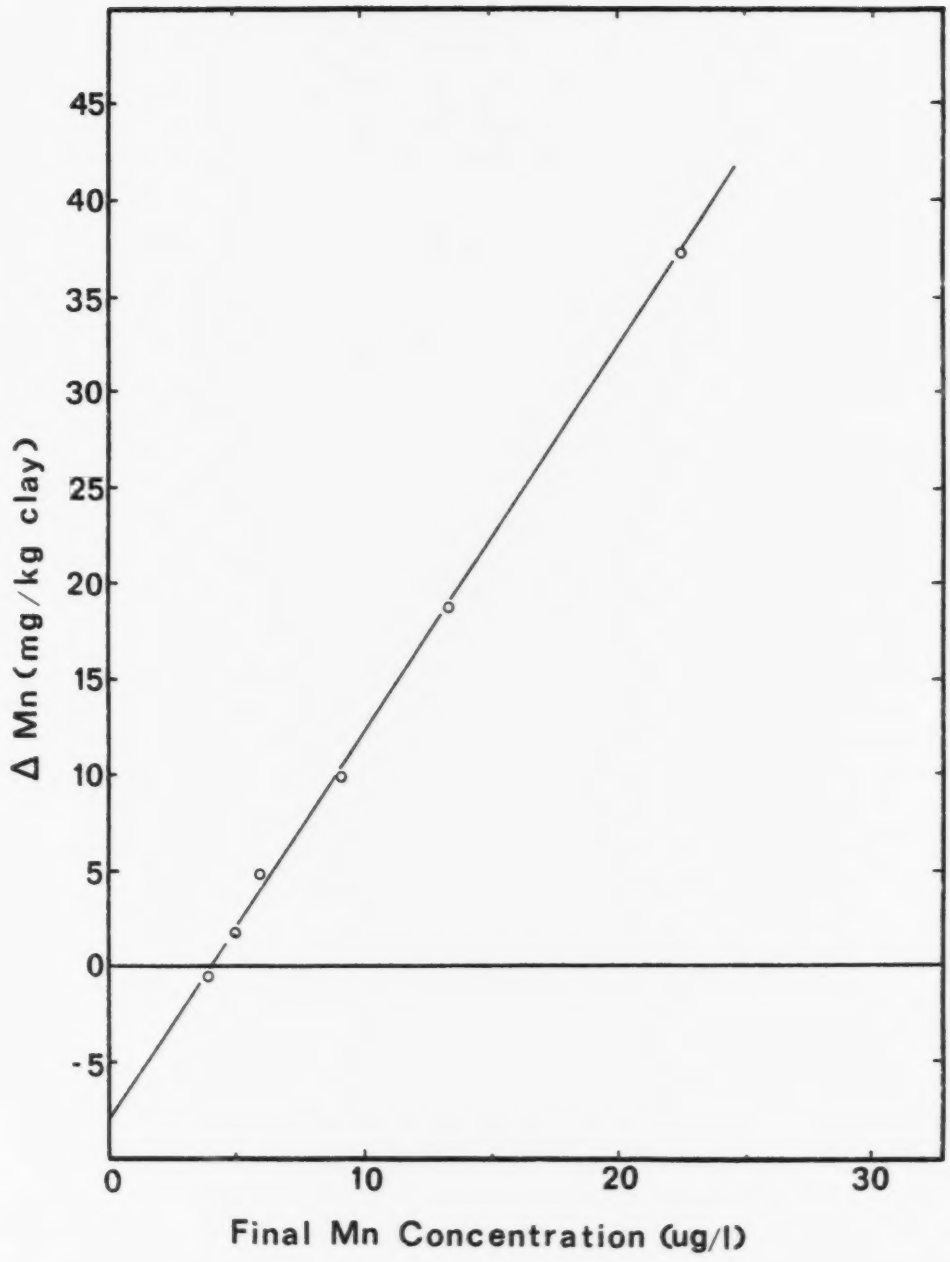

Figure 7. Manganese sorption isotherm for clay soil in Lake Superior water.

The data in Figure 6 show that copper has little tendency to be released from the clay. This particular sample would remove copper from solution in lake water down to approximately one µg/l in copper concentration. The data in Table 20 shows a possible small release of copper projected from the leaching of the LS-5 soil sample. This indicates that the value in Table 20 for copper is very sensitive to errors in the copper determination, as a change of 2 µg/l in concentration of the leachate could change the indicated release to an apparent adsorption by the clay. The data in Figure 6 also shows the ability of the clay particles to remove copper from Lake Superior water under conditions of higher copper ion concentration. For example, the soil sample suspended in Lake Superior water at a concentration of 10 µg/l copper would result in a removal of 350 grams of copper per ton of the clay. This ability of the soil to remove copper was also demonstrated by the data in Table 19.

The data in Figure 7 shows that the clay soil sample will remove manganese from solution if the concentration of the manganese is greater than about 4 µg/l. Since Lake Superior water contains about 0.2 µg/l of manganese, a net release of manganese from the soil should occur. At a lake water concentration of 0.2 µg/l, the data indicates a release of about 7 grams of manganese per metric ton of clay. For 8×10^6 metric tons of eroded soil, the total release would be 56 metric tons. The exchange-studies method (Figure 7) gives a manganese release value as if the clay were leached in 0.2 µg/l manganese solution without any increase in concentration as it is released and this situation would better approximate lake conditions. However, if the concentration of manganese in the water is greater than 0.2 µg/l, then the release would be a lesser amount. Some limited data on iron exchange with clay in aqueous suspensions indicates that the value in Table 20 is not too small.

The values in Table 20 should give the magnitudes of release expected for the various metals from the clay samples. In general the releases are small and, in many cases, they could only be listed as "less than" values. In order to obtain more accurate values on the metal exchange capacity with clay samples, much data would have to be collected using a more sensitive analytical technique in order to allow a statistical treatment for confidence levels. Also, data would have to be collected on the effects of clay-to-solution ratio in the exchange capacity of the clays.

EXCHANGE OF PHENOLICS WITH CLAYS

Experimental Procedure

This phase of the study focused on the ability of clay particles to affect the concentrations of phenolic-type compounds in aqueous solution. In the study area, phenolics are particularly associated with the St. Louis River (largest Lake Superior tributary whose waters enter the lake at Duluth, Minnesota) and the Duluth-Superior Harbor area. Two sampling surveys of the St. Louis River and Duluth-Superior Harbor were enacted in order to establish the total phenolic levels for these waters. Samples from a site exhibiting the highest phenolic concentration were spiked with various amounts of clay

soil (LS-5), and the decrease in total phenolics compared to a sample blank (no clay) was measured. Measurements of the clay interactions with the phenolic-type components of the natural waters was also studied as a function of time.

2,4-dichlorophenol was used as a representative phenolic-type compound in further investigations of clay-phenol interactions. These interactions were studied as a function of time, initial concentration of 2,4-dichlorophenol, and soil-to-solution ratio.

Results and Discussion

The results of the two surveys for total phenolics are given in Table 21. Values in the 20 to 114 µg/l range were found for the two sampling dates, with the Interstate 35 sampling site near Cloquet, Minnesota showing the highest values for each survey.

Water obtained on July 22 from the Interstate 35 sampling site was used in a study of the interactions of the LS-5 soil sample with the phenolics in the sample. Various amounts of clay (0.2 to 1.2 g) were added to 500 ml of the river water. The suspensions were shaken for 30 minutes and filtered through Gelman type-A glass fiber filters and analyzed for total phenolics. The results are shown in Table 22.

Studies involving the addition of approximately 0.42 grams of clay soil to 500 ml solutions of 0.5 mg/l 2,4-dichlorophenol were carried out by analyzing the suspensions for 2,4-dichlorophenol as a function of time. The results showed no difference in phenol concentration between 30-minute, 90-minute, and 150-minute equilibration times. Consequently, a 30-minute equilibration time was used in the studies. 500 ml solutions containing an initial concentration of 0.5 mg/l 2,4-dichlorophenol were spiked with clay soil in the range of 0.2 g to 0.8 g. After an equilibration time of 30 minutes, the solutions were analyzed for 2,4-dichlorophenol. The experiment was repeated using an initial concentration of one mg/l 2,4-dichlorophenol. These data are also shown in Table 22.

The data in Table 22 indicate a significant reduction in total phenolic concentration with the addition of clay soil to the water. A solution which is about 400 mg/l in clay results in a 11% phenolic reduction (expressed as weight of phenol) whereas the 2400 mg/l clay suspension experiences a 81% reduction. Similar reductions in the concentration of 2,4-dichlorophenol occur. In this case, there is an increased reduction by weight but a similar reduction in terms of equivalent moles of phenol. A slightly greater amount of 2,4-dichlorophenol is removed from the one mg/l solution than the 0.5 mg/l solution.

It is concluded that the suspended clay particles do decrease the concentration of phenolic-type compounds in aqueous solution. The fate of the adsorbed phenolic molecules in terms of possible decomposition or transport has not been considered here.

TABLE 21: TOTAL PHENOLICS IN NATURAL WATERS

Sample Location	µg per liter of total phenolics	
	June 17, 1975	July 22, 1975
Superior Harbor Entry (Superior, WI)	30	31
Barker's Island (Superior Harbor)	37	41
Arrowhead Bridge (St. Louis Harbor)	20	90
Huron Cement (Superior Harbor)	34	62
Blatnik Bridge (St. Louis Harbor)	35.5	39
Drill's Marina (St. Louis River)	51	55
Interstate 35-Cloquet (St. Louis River)	70.5	114

TABLE 22: INTERACTIONS OF CLAY WITH PHENOLICS*

Sample: St. Louis River Water-Interstate 35 Near Cloquet

Weight of Clay (g)	Initial Total Phenolics (µg/l)	Final Total Phenolics (µg/l)	Micrograms Phenol Adsorbed per gram of Soil
0.2007	116	103	65
0.4003	116	82	85
0.6027	116	57.5	96
0.8044	116	47.5	85
1.0024	116	28	88
1.2054	116	22	78

Sample: 500 µg/l 2,4-dichlorophenol

Weight of Clay (g)	Final 2,4-dichlorophenol Concentration (µg/l)	Micrograms 2,4-dichlorophenol Adsorbed per gram of Soil
0.2022	435	161
0.2057	460	97
0.2033	456	108
0.2082	455	108
0.3008	410	150
0.3017	405	157
0.4119	363	166
0.4133	384	140
0.5028	329	170
0.5053	330	168
0.7192	280	153
0.7006	286	153

Sample: 1000 µg/l 2,4-dichlorophenol

Weight of Clay (g)	Final 2,4-dichlorophenol Concentration (µg/l)	Micrograms 2,4-dichlorophenol Adsorbed per gram of Soil
0.2054	920	190
0.2080	915	200
0.4038	848	190
0.4109	840	195
0.6050	763	196
0.6012	775	187
0.8058	720	174

*All solutions were 500 ml in volume.

SECTION 7

CHEMISTRY OF LAKE SUPERIOR WATER SAMPLES AS RELATED TO TURBIDITY

GENERAL PROCEDURES

A sampling network was chosen in a near-shoreline region of western Lake Superior for monitoring suspended solids and numerous chemical parameters. The region selected was approximately one mile (1.6 km) west of Bardon Creek (Figure 1). This sampling location is approximately 15 miles (24 km) from the Duluth-Superior metropolitan area and thus the water composition should be minimally influenced by any point source discharge from this area. Water sampling was carried out as a function of depth at 10, 20, 40, 60, and 80-foot depth profiles. In addition, sediment coring was attempted in this region. The cores obtained showed that the lake bottom in this region is mainly composed of sand, even out to an 80-foot (24.4 m) depth. Consequently only a few cores were taken in this region.

The purpose of this sampling network was to monitor suspended solids and water chemistry as a function of weather events. This monitoring would provide additional information relating to the degree of turbidity of the water resulting from different types of wind and precipitation events and data on settling times for the suspended matter. The water chemistry would give field observations relating to chemical changes which occurred during periods of high turbidity.

The water samples were obtained using a Van Dorn-type plastic water sampler. The sampling network consisted of sampling at five feet below the surface at a 10-foot water depth (sample 10-5); at 3 and 18 feet below the surface at a 20-foot water depth (samples 20-3 and 20-18); at 3, 20, and 38 feet below the surface at a 40-foot water depth (samples 40-3, 40-20, and 40-38); at 3, 30, and 58 feet below the surface at a 60-foot water depth (samples 60-3, 60-30, and 60-58); and at 3, 40, and 78 feet below the surface at an 80-foot water depth (samples 80-3, 80-40, and 80-78). At the 80-foot depth profiles, the perpendicular distance to the shoreline was approximately four miles.

RESULTS AND DISCUSSION

The only significant weather event occurred at the beginning of June. This event consisted of strong easterly winds (10 to 25 mph) with less than 0.5 inches (1.3 cm) of precipitation on June 4 and 2.5 inches (6.4 cm) of rain over the period June 11 to June 12. The remainder of the summer was void of any significant weather events which would cause high turbidity

levels on the lake. Consequently only two water samplings were obtained under turbid water conditions, and this turbidity was confined to the near-shoreline region of the lake. A total of eight samplings were carried out at the Bardon Creek-area Lake Superior site in June, July, and August. Except for the June 6 and June 14 sampling times, the waters were relatively low in suspended solids. The suspended-solid values found for the sampling grid pertaining to these eight surveys are summarized in Table 23. A comparison of the June 26 suspended-solid values to those obtained on June 14 indicates that the concentration of suspended solids had decreased in the area by a factor of 2 to 4 in 12 days. This is an approximate agreement with the observations reported by Sydor[2] for particle settling under laboratory conditions.

Chemical analyses were performed on water samples obtained on June 6, June 26, July 17, and August 15. These results are presented in Tables 24 through 27. Most of these water samples contained relatively low suspended-solids concentrations with only one sample containing greater than 100 mg/l concentration. Therefore the differences in suspended solids in the samples are not large enough to make accurate correlations of water chemistry to turbidity. At this time, no statistical analysis of the data has been performed. A general survey of the data would indicate an increase in total dissolved solids, total phosphorus, total soluble phosphorus, orthophosphate, particulate iron, and sodium at times when the waters contain higher suspended solids. No doubt, the degree of mixing of the waters and currents is important in determining the values of most of the chemical parameters.

Previous work along the shoreline region of Northern Wisconsin has indicated generally higher values for specific conductance, alkalinity, hardness, calcium, magnesium, sodium, iron, orthophosphate, and chemical oxygen demand in this area compared to Minnesota shoreline values.[12] A chemical analysis of the waters the day following a severe weather event (wind and/or wind-precipitation) would be needed to establish values of the chemical parameters under high-turbidity conditions. Most of the data presented here would serve to establish chemical values at lower suspended solid conditions.

TABLE 23: LAKE SUPERIOR BARDON CREEK-AREA SUSPENDED SOLIDS PROFILES

SUSPENDED SOLIDS (ug/l)

DATE	10-5	20-3	20-17	40-3	40-20	40-37	60-3	60-30	60-57	80-3	80-40	80-77
6/6	122	62	35	--	13	5	3	2	1.5	--	---	---
6/14	80	33	23	13	17	21	5	39	11	0.5	8	12
6/26	21.5	11	11.5	8	6	6	8	2	2	--	---	---
7/5	14	15	20	4	11	9	1	2	2	1	1	3
7/9	15	16	13	4	4	2	2	4	2	3	1	1
7/17	6	6	6	2	2	2	2	2	1	2	1	2
7/24	9	4	1	2.5	1	2	2	2	1	1	.5	2
8/15	7	3	3	2	1	4	1	2	2	1	2	2

TABLE 24: LAKE MONITORING IN POPLAR RIVER - BARDON CREEK AREA

DATE: June 6, 1975

Profile (ft.)	10	20	20	40	40	40	60	60	60
Depth (ft.)	5	3	18	3	20	38	3	30	58
Suspended Solids (mg/l)	122	62	35		13	5	3	2	1.5
pH	7.75	7.54	7.53	7.51	7.42	7.38	7.38	7.42	7.39
Specific Conductance*	105.3	105.0	103	98.6	98.6	96.6	98.9	96.3	96.6
Dissolved Oxygen (mg/l)	9.6	10.2	9.6	10.8	10.9	10.9	11.4	11.5	11.5
Total P (µg/l)	29	26	14	10	15	8	12	8	5
Total Soluble P (µg/l)	16	8	2	3	<1	5	3	4	<1
Orthophosphate (µg PO_4/l)	27	16	8	10	3	7	1	4	2
Alkalinity (mg $CaCO_3$/l)	47.2	44.4	42.9	40.7	41.0	41.6	41.0	40.8	40.8
Silica (mg/l)	3.14	3.46	3.06	3.16	3.20	3.27	3.04	3.26	3.24
Nitrate (mg/l)	0.84	0.95	0.85	0.91	0.87	0.93	0.97	1.02	1.23
Kjeldahl N (mg/l)	0.25	0.42	0.2	0.27	0.10	0.23	0.16	0.05	0.27
Colorimetric Soluble Fe (µg/l)	86	69	54	53	47	42	37	24	24
Atomic Absorption Soluble Fe (µg/l)		124	45						
Particulate Fe (µg/l)	1420	1030	750	140	170	200	43	70	100
Sodium (mg/l)	2.6	3.3	2.3	2.9	2.3	2.0	1.9	2.0	3.4
Potassium (mg/l)	0.72	0.71	0.69	0.67	0.60	0.72	0.62	0.58	0.63
Calcium (mg/l)	12.7	12.8	15.8	11.9	12.8	13.5	15.1	11.4	12.6
Magnesium (mg/l)	3.4	3.4	3.2	3.3	3.0	3.1	3.1	3.1	3.1
Chloride (mg/l)	3.4	2.0	2.0	4.6	3.3	1.8	1.8	1.7	1.7
Copper (µg/l)	5	5	5	5	5	4	6	5	4
Manganese (µg/l)	8.3	6.7	5.3	5.1	4.2	2.4	2.5	3.4	2.6
Cadmium (µg/l)	0.3	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.3
Zinc (µg/l)	7	1	3	6	6	2	3	1	8
Lead (µg/l)	2	<1		7	3	<1	3		7

*Micromhos/cm

TABLE 25: LAKE MONITORING IN POPLAR RIVER - BARDON CREEK AREA

DATE: June 26, 1975

Profile (ft.)	10	20	20	40	40	40	60	60	60
Depth (ft.)	5	3	18	3	20	38	3	30	58
Suspended Solids (mg/l)	21	11	11	8	6	6	8	2	2
pH	7.48	7.45	7.46	7.49	7.42	7.41	7.49	7.47	7.44
Specific Conductance*	102.7	101.7	102.0	100.0	100.0	100.0	100.8	98.6	98.3
Dissolved Oxygen (mg/l)	10.9	11.0	10.9	11.0	11.4	11.2	10.9	12.0	12.1
Total P (µg/l)	28	23	39	9	18	13	21	17	8
Total Soluble P (µg/l)	1	<1	5	5	<1	3	5	3	4
Orthophosphate (µg PO_4/l)	11	4	2	6	11	6	7	4	11
Alkalinity (mg $CaCO_3$/l)	45.4	44.6	44.5	44.3	45.4	44.4	44.4	43.8	44.6
Silica (mg/l)	2.81	3.17	2.88	2.98	2.91	2.92	2.93	2.75	2.26
Nitrate (mg/l)	0.97	0.92	0.96	0.90	0.99	0.96	0.95	1.02	1.00
Kjeldahl N (mg/l)		0.03		0.07			0.10		
Colorimetric Soluble Fe (µg/l)	36	30	41	52	30	34	63	55	8
Particulate Fe (µg/l)	440	280	330	270	180	120	140		62
Sodium (mg/l)	1.4	1.3	1.7	2.0	1.6	1.9	1.9	1.3	1.7
Potassium (mg/l)	0.63	0.75	0.72	0.67	0.65	0.71	0.71	0.64	0.54
Calcium (mg/l)	14.0	13.8	14.5	14.0	14.2	14.2	14.9	14.6	13.9
Magnesium (mg/l)	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.3	3.3
Chloride (mg/l)	1.5	1.5	1.7	2.0	1.7	1.6	1.7	1.6	1.2
Copper (µg/l)	2	2	2	2	1	1.5	1	1	1
Manganese (µg/l)	2.8	1.5	2.0	1.9	1.9	1.5	2.5	2.1	0.5
Cadmium (µg/l)	<0.1		<0.1		<0.1				
Zinc (µg/l)	2	2	7	2	2	2	2	3	2
Lead (µg/l)		<1	<1		<1		<1	<1	

*Micromhos/cm

TABLE 26: LAKE MONITORING IN POPLAR RIVER - BARDON CREEK AREA

DATE: July 17, 1975

Profile (ft.)	10	20	20	40	40	40	60	60	60	80	80	80
Depth (ft.)	5	3	18	3	20	38	3	30	58	3	40	78
Suspended Solids (mg/l)	6	6	6	2	2	2	2	2	1	2	1	2
pH	7.61	7.58	7.59	7.69	7.70	7.40	7.61	7.40	7.43	7.79	7.35	7.40
Specific Conductance*	101.2	100.5	100.8	99.8	100.1	98.9	100.5	98.6	95.7	100.1	96.0	96.3
Dissolved Oxygen (mg/l)	---	9.2	8.7	9.0	9.0	10.3	9.1	10.1	---	-----	11.8	11.6
Total P (µg/l)	15	10	5	6	5	3	5	17	1	10	3	<1
Total Soluble P (µg/l)	3	6	2	10	8	5	-----	3	<1	<1	<1	<1
Orthophosphate (µg PO_4/l)	8	<1	3	<1	12	2	<1	10	4	6	20	<1
Alkalinity (mg $CaCO_3$/l)	43.1	43.3	---	44.0	44.6	44.6	43.1	44.2	43.3	44.8	44.3	43.6
Silica (mg/l)	2.82	2.93	3.06	2.68	2.74	3.08	2.77	2.80	3.05	2.76	3.11	2.91
Nitrate (mg/l)	0.92	0.76	0.90	---	0.79	1.21	0.89	1.01	1.23	0.84	1.14	1.26
Kjeldahl N (mg/l)	0.12	0.15	---	---	0.05	---	-----	0.11	---	-----	-----	-----
Atomic Absorption Soluble Fe (µg/l)	68	74	62	62	-----	---	89	-----	---	76	-----	-----
Colorimetric Soluble Fe (µg/l)	74	79	65	55	57	44	72	27	14	75	14	11
Particulate Fe (µg/l)	145	165	135	67	93	55	76	100	64	76	90	92
Sodium (mg/l)	2.0	1.8	1.7	2.2	1.9	1.8	1.8	2.2	1.7	2.0	1.4	1.5
Potassium (mg/l)	0.86	0.83	0.82	0.73	0.78	0.75	0.80	0.77	0.73	0.77	0.72	0.73
Calcium (mg/l)	14.2	14.1	14.3	14.1	14.5	14.5	14.0	14.2	14.0	14.0	13.9	14.4
Magnesium (mg/l)	3.6	3.5	3.5	3.6	3.6	3.5	3.5	3.4	3.4	3.5	3.3	3.4
Chloride (mg/l)	1.9	1.8	1.7	1.7	1.5	1.4	1.8	1.5	1.3	1.8	1.2	1.3
Copper (µg/l)	11	8	6	3	3	4	5	4	4	3	3	3
Manganese (µg/l)	5	7	6	20	2	1	4	3	3	5	2	3
Zinc (µg/l)	17	10	11	7	4	4	10	8	4	6	4	8
Cadmium (µg/l)	1.3	0.5	0.7	0.3	0.1	0.3	0.2	0.2	0.2	0.1	0.2	0.2
Lead (µg/l)	2.5	1.5	1.5	2	0.5	2	1.5	1	<0.5	0.5	0.5	0.5

*Micromhos/cm

TABLE 27: LAKE MONITORING IN POPLAR RIVER - BARDON CREEK AREA

DATE: August 15, 1975

Profile (ft.)	10	20	20	40	40	40	60	60	60	80	80	80
Depth (ft.)	5	3	18	3	20	38	3	30	58	3	40	78
Suspended Solids (mg/l)	7	3	3	2	1	4	1	2	2	1.5	2	2
pH	7.73	7.73	7.62	7.77	7.78	7.43	7.75	7.58	7.48	7.75	7.60	7.39
Specific Conductance*	99.5	98.1	98.1	96.3	96.0	98.6	96.0	96.0	96.0	96.3	96.7	95.8
Dissolved Oxygen (mg/l)	5.1	6.0	11.0	8.2	9.6	7.6	9.6	9.0	6.8	9.1	11.0	12.1
Total P (µg/l)	12	9	7	5	7	9	5	7	9	6	9	8
Total Soluble P (µg/l)	5	5	4	3	3	5	3	3	6	3	4	5
Orthophosphate (µg PO_4/l)	7	14	11	9	10	5	6	6	9	5	12	9
Alkalinity (mg $CaCO_3$/l)	49.0	48.0	48.2	46.0	46.7	48.7	46.8	47.9	45.7	50.0	48.2	44.3
Silica (mg/l)	2.49	2.52	2.44	2.52	2.47	2.85	2.61	2.71	2.88	2.55	2.81	3.20
Nitrate (mg/l)	0.67	0.78	0.64	0.83	0.70	0.87	0.72	0.73	1.05	0.86	0.97	0.99
Kjeldahl N (mg/l)	0.27	0.24	0.26	0.19	---	0.18	0.18	---	0.15	0.18	---	---
Total Fe (µg/l)	202	119	112	275	34	108	48	68	70	102	97	60
Atomic Absorption Soluble Fe (µg/l)	50	57	42	20	23	37	33	32	20	21	34	13
Sodium (mg/l)	1.6	1.7	1.7	1.7	1.7	1.6	1.6	1.6	1.5	1.6	1.6	1.4
Potassium (mg/l)	0.62	0.60	0.59	0.58	0.58	0.60	0.57	0.59	0.57	0.58	0.57	0.58
Calcium (mg/l)	14.0	13.3	14.0	13.9	13.5	14.0	13.5	13.4	13.5	14.0	13.3	13.2
Magnesium (mg/l)	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.2	3.3	3.3	3.2
Chloride (mg/l)	1.6	1.3	1.6	1.6	1.4	1.5	1.4	1.5	1.3	1.4	1.4	1.3
Copper (µg/l)	4	2	2	3	2	2	2	2	2	2	3	1
Manganese (µg/l)	8	4	3	1	3	2	2	1	1	1	7	2
Zinc (µg/l)	6	3	3	3	2	2	3	3	2	2	3	1
Cadmium (µg/l)	0.05	0.06	0.07	0.02	0.05	0.02	0.02	0.15	0.02	0.02	0.05	0.02
Lead (µg/l)	<0.2	<0.2	0.8	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.3	0.2	<0.2
Aluminum (µg/l)	19	31	22	5	11	23	9	12	11	5	15	10

*Micromhos/cm

SECTION 8

RIVER MONITORING FOR SEDIMENT LOADS

GENERAL PROCEDURES

In cooperation with Dr. Michael Sydor, this phase of the study focused on spring monitoring of river discharges, concentrations and particle-size distributions of sediment loads, and a determination of the sediment input to Lake Superior from northern Wisconsin streams during spring runoff. The study area included Lake Superior tributaries from Superior, Wisconsin to Cornucopia, Wisconsin (Figure 1). The eastern half of this shoreline area was monitored by University of Wisconsin-Superior staff while the western half was sampled by staff from the University of Minnesota-Duluth. In this section, a summary of the results of the University of Wisconsin study will be given.

Sampling sites on the streams were established at accessible points close to the stream mouths but at a distance from Lake Superior, which would avoid backwash from the lake during seiche conditions. Suspended-solid measurements were made by obtaining depth-integrated samples at vertical profiles across the river or creek (U.S. DH-48 or U.S. DH-59 samplers were used). Stream-velocity measurements were obtained at two depths along each profile using a Gurley meter. Cross-sectional area parameters (depths, width of stream) were measured at each time of sampling. Suspended solids in the water samples were measured by collecting the solids on tared 0.45-micron membrane filters. Turbidity measurements were made by the staff at the University of Minnesota-Duluth.

RESULTS

The discharge and sediment load data for Bayfield County, Wisconsin streams are summarized in Table 28. These data have been used by Dr. Sydor in conjunction with other data to estimate the total annual tributary input of suspended solids to Lake Superior for Douglas and Bayfield Counties. These estimates have been summarized in the introduction of this report (Section 1).

The major conclusion drawn from these runoff data is that the input of suspended solids from Bayfield County streams is much smaller compared to the Douglas County input. The Nemadji River (Douglas County) contributes 89% of the total stream eroded material in the two counties.[3] For Bayfield County streams investigated in this study, the Bois Brule, Iron, Flag, and Cranberry Rivers contribute the highest sediment loads during spring runoff. The Flag

River showed the highest sediment load on a given day (416 metric tons/day on April 23).

TABLE 28: DISCHARGES AND SEDIMENT LOADS OF LAKE SUPERIOR TRIBUTARIES (1975)

Brule River at Bridge East of Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 11	9.2	7.0	6.1
April 14	9.9	10.2	60
April 17	12.3	17.6	102
April 22	12.5	17.7	82
April 24	12.8	20.2	58
April 28	13.8	17.5	40
April 30	12.3	17.8	47
May 2	13.6	19.0	32
May 7	12.6	14.0	31

Cranberry River 1/2 mile From Mouth

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 10	1.7	1.5	0.4
April 13	3.0	1.8	5.7
April 16	4.1	3.3	25.4
April 21	3.5	2.4	8.9
April 23	5.7	5.1	262
April 25	2.2	1.4	5.0
April 29	3.3	1.8	12.5
May 1	2.5	1.4	4.2
May 5	2.5	1.5	3.9
May 9	1.8	1.3	1.6

First Creek East of Flag River

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 13	0.06	0.07	<0.5
April 16	0.20	0.25	5.3
April 21	0.13	0.12	0.9
April 23	0.20	0.25	16.4
April 25	0.12	0.09	0.6
April 29	0.12	0.11	1.7
May 1	0.09	0.03	0.2
May 5	0.06	0.02	0.1

TABLE 28: DISCHARGES AND SEDIMENT LOADS OF LAKE SUPERIOR TRIBUTARIES (1975) (CONTINUED)

Fish Creek On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 14		ice covered	
April 17		ice covered	
April 22	13.7	1.7	9.4
April 24	14.0	1.9	21
April 29	16.9	2.6	26
May 1	12.0	0.5	2.0
May 7	14.1	<0.2	<0.5

Iron River

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 11		ice covered	
April 17	91.5	27.5	270
April 22	77.8	17.0	104
April 24	93.9	5.0	25.3
April 28	87.1	12.1	76.5
May 7	95	<1.0	<5

First Creek East of Jardines

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 13	0.77	0.17	0.6
April 16	0.74	0.59	3.5
April 21	0.43	0.32	0.6
April 23	0.64	0.57	2.3
April 25	0.36	0.11	0.2
April 29	0.53	0.29	0.8
May 1	0.22	0.33	0.2
May 5	0.23	0.07	0.1

TABLE 28: DISCHARGES AND SEDIMENT LOADS OF LAKE SUPERIOR TRIBUTARIES (1975) (CONTINUED)

Flag River On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 10	5.3	1.6	1.2
April 13	8.7	3.5	29
April 16	14.3	9.8	100
April 21	8.8	4.7	34
April 23	14.6	12.8	416
April 25	5.7	2.5	13
April 29	9.5	7.8	112
May 1	6.0	3.2	30
May 5	6.0	2.2	10
May 9	4.9	1.3	2.6

Haukkala Creek

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 15	1.2	2.3	53
April 18	0.77	1.5	36
April 23	1.9	0.74	7.3
April 25	1.4	0.26	1.8
April 30	2.3	0.98	3.1
May 2	1.2	0.26	1.3
May 9	0.77	0.03	0.2

Jardines Creek On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 13	1.2	0.89	4.8
April 16	2.7	2.9	17.2
April 21	2.3	0.62	2.9
April 23	4.0	1.8	14.1
April 25	1.7	0.68	2.1
April 29	2.1	1.4	11.7
May 1	1.3	0.64	0.9
May 5	1.3	0.30	0.8

TABLE 28: DISCHARGES AND SEDIMENT LOADS OF LAKE SUPERIOR TRIBUTARIES (1975) (CONTINUED)

Nelson Creek On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 10		ice covered	
April 14		ice covered	
April 15	1.7	1.3	6.9
April 18	1.3	1.8	20.6
April 23	1.3	0.85	3.8
April 25	1.0	0.38	1.1
April 30	1.1	0.52	2.2
May 2	0.77	0.21	0.5
May 9	0.58	0.07	0.3

Reefer Creek On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 14		ice covered	
April 17		ice covered	
April 22	15.1	2.1	13.9
April 24	15.5	3.7	22.9
April 28	18.5	1.0	7.4
May 1	14.3	0.75	3.5
May 7	15.0		<0.5

Trask Creek On Highway 13

Date	Cross-Sectional Area (m^2)	Total Discharge (m^3/sec)	Suspended Solids Load (tons/day)
April 11		ice covered	
April 14	3.8	2.2	10
April 18	9.0	2.3	56.4
April 22	2.6	0.88	5.9
April 24	3.3	1.2	4.8
April 28	2.7	0.73	5.1
April 30	3.6	1.1	9.0
May 2	2.8	0.24	1.1
May 7	2.4	0.10	0.3

SECTION 9

SUMMARY OF CHEMICAL INPUTS TO LAKE SUPERIOR

The phase of this study dealing with the chemical inputs to Lake Superior from the red clays by soil leaching, sediment resuspension, and river particulate leaching has been reported in the previous sections of this report. This information will be summarized here with a brief discussion of the results.

The chemical input to Lake Superior due to leaching of resuspended sediments has not been previously tabulated for some of the parameters, and this information is listed here in Table 29. These results are based on the data in Table 6 with the uncertainties estimated from the statistical analysis presented in Appendix B.

The total inputs of the chemical parameters determined during the course of this study are given in Table 30 along with the contributions from the various sources. The contributions from leaching of resuspended sediments are not included in the total inputs listed since much of this contribution would occur even without resuspension due to the normal flux from the sediments. In addition, the values for shoreline erosion include contributions from seven weeks of leaching (for the parameters down to magnesium in Table 30 and 3 months for silica) and therefore it is difficult to separate into a soil and sediment contribution because of the uncertainty when the suspended particles become sediment. Also there is a fairly large uncertainty in the amount of resuspended material particularly during the winter months.[3]

The uncertainties in the inputs listed in Table 30 are based on uncertainties in the chemical analysis (see Appendix B) and assume no errors in the amounts of clay material eroded. If the values for the magnitude of particulate material carried into Lake Superior are revised, the values in Table 30 could also be easily corrected.

The results indicate conclusively that shoreline erosion of clay soils makes a larger contribution than sediment resuspension and river particulates to chemical inputs to Lake Superior for all parameters for which values are obtained. Data was not obtained in this study for leaching of Nemadji River particulates in terms of trace metals, iron, and aluminum although in most cases the values probably are not large compared to inputs from soil erosion. The data shows that although the interstitial water of the clay-bearing sediments are enriched in certain of the chemical parameters, the contribution of the release of this water during turbulence events is not important in terms of enriching Lake Superior waters in the chemical parameters. However,

TABLE 29: CHEMICAL INPUTS DUE TO LEACHING OF RESUSPENDED SEDIMENT*

Parameter	Chemical Release (mg parameter per gram of sediment)	Inputs to Lake Superior (metric tons/year)
Dissolved Solids**	12.8 ± 1.6	20,500 ± 2,400
Alkalinity**	10.3 ± 0.8	16,500 ± 1,200
Orthophosphate (PO_4)**	0.063 ± 0.027	100 ± 40
Total Soluble P**	0.023 ± 0.03	37 ± 4
Nitrate**	0.38 ± 0.25	610 ± 380
Total Kjeldahl N***	<0.2	<320
Sodium†	0.06 ± 0.04	96 ± 60
Potassium**	0.24 ± 0.11	380 ± 160
Calcium†	0.6 ± 0.4	960 ± 600
Magnesium†	0.30 ± 0.20	480 ± 300
Silica††	2.76 ± 0.50	4,500 ± 750

*Based on 1.6×10^6 metric tons/yr of suspended sediment.
**Based on data from Table 6.
***Based on lake water and DC-1 sediment leachate sample analysis by EPA Region V Laboratory after 7 weeks of leaching at 23-27°C and 4°C.
†Based on data in Table 8.
††Based on data in Table 7.

TABLE 30: CHEMICAL INPUTS TO LAKE SUPERIOR DUE TO SOIL EROSION, RIVER PARTICULATES, AND SEDIMENT RESUSPENSION[1]

Parameter	Shoreline Erosion[2]	Sediment Resuspension (leaching)[4]	Sediment Resuspension (Interstitial Waters)[5]	River Particulates[6]	Total Inputs[7]
Dissolved Solids	192,000 ± 40,000	20,500 ± 2,400	------	14,900 ± 1,900	207,000 ± 42,000
Alkalinity	184,000 ± 40,000	16,500 ± 1,200	------	13,000 ± 1,900	197,000 ± 42,000
Orthophosphate (PO_4)	240 ± 80	100 ± 40	0.0045	58 ± 17	298 ± 97
Total Soluble P	280 ± 160	37 ± 4	------	23 ± 12	303 ± 172
Nitrate (NO_3)	400 ± 400	610 ± 380	------	1,100 ± 580	1,500 ± 1,000
Chloride	<800	--------	------	--------	<800
Total Kjeldahl N	<1600	<320	------	<175	<1800
Sodium	2,000 ± 1,600	96 ± 60	2.0	--------	2,000 ± 1,600
Potassium	3,400 ± 1,200	380 ± 160	1.0	93 ± 74	3,500 ± 1,300
Calcium	48,000 ± 24,000	960 ± 600	13	--------	48,000 ± 24,000
Magnesium	7,200 ± 3,200	480 ± 300	3.6	580 ± 380	7,800 ± 3,600
Silica	14,400 ± 3,200	4,500 ± 750	9.5	--------	14,400 ± 3,200
Copper	<2	<1.0	0.002	--------	<2
Manganese[3]	56 ± 30	0.4	0.45	--------	56 ± 30
Cadmium	<0.008	<0.01	0.0005	--------	<0.008
Zinc	<8	<0.6	0.004	--------	<8
Lead	<1	<0.2	0.004	--------	<1
Chromium	<0.1	--------	------	--------	<0.1
Nickel	<8	<1.5	------	--------	<8
Aluminum	76 ± 50	<7.5	0.05	--------	76 ± 50
Iron	64 ± 10	<11	0.045	--------	64 ± 10
Mercury	<0.08	<0.01	------	--------	<0.08
Arsenic	<2	<0.25	------	--------	<2
Selenium	<4	<0.7	------	--------	<4

[1]Metric tons per year.
[2]From data in Tables 10 and 20.
[3]Based on chemical exchange data (Section 6).
[4]Based on data in Tables 20 and 28.
[5]Based on data in Table 18.
[6]Based on data in Table 10. Values taken as 35% higher than the inputs of Nemadji River.
[7]Includes inputs from shoreline erosion, sediment resuspension (interstitial waters), and river particulates. No values available for heavy metal plus iron and aluminum for river particulates.

the enrichment may be important in the effects on bottom-feeding species in Lake Superior.

The values of Table 30 would have to be compared to inputs from industrial, municipal, tributary (chemical parameters dissolved in river waters) and atmospheric sources along with chemical fluxes from Lake Superior sediments to determine the significance of chemical inputs on Lake Superior due to erosion and resuspension of red clay material.

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APPENDIX A

Data For Seven-Week Clay-Leaching Experiments as Described in Section 4.

TABLE A-1: pH OF CLAY LEACHATES AND SAMPLE BLANKS

	DAYS LEACHED					
Sample*	Initial	1	7	21	35	49
1	7.35	7.70	7.68	7.60	7.59	7.60
2	7.35	7.77	7.72	7.68	7.63	7.70
3	7.35	7.75	7.72	7.71	7.74	7.73
4	7.35	7.73	7.70	7.70	7.71	7.73
5	7.35	7.73	7.75	7.79	7.75	7.75
6	7.35	7.76	7.76	7.79	7.75	7.75
7	7.35	7.79	7.81	7.79	7.79	7.77
8	7.35	7.50	7.55	7.60	7.50	7.54
9	7.41	7.38	7.13	7.59	7.55	7.58
10	7.41	7.43	7.48	7.59	7.50	7.60
11	7.41	7.44	7.40	7.50	7.55	7.59
12	7.41	7.50	7.46	7.49	7.40	7.56
13	7.41	7.65	7.55	7.75	7.60	7.70
14	7.41	7.63	7.62	7.79	7.70	7.70
15	7.41	7.71	7.64	7.79	7.70	7.70
16	7.41	7.72	7.69	7.80	7.62	7.70
17	7.40	7.60	7.55	7.40	7.53	7.59
18	7.40	7.50	7.51	7.49	7.62	7.70
19	5.90	8.79	8.27	8.60	8.26	7.95
20	5.90	8.71	8.59	8.59	8.42	7.70
21	5.90	6.00	6.11	5.89	6.02	6.45
22	7.40	7.57	7.63	7.50	7.65	7.77
23	7.40	7.79	7.80	7.73	7.79	7.79
24	7.40	7.60	7.70	7.64	7.73	7.79
25	5.99	5.99	6.01	5.69	5.66	5.78
26	5.70	5.70	5.99	5.71	5.71	5.62
27	5.43	5.43	7.50‡	5.30	5.39	5.51
28	5.39	5.39	5.61	5.04	5.38	5.20
29	7.44	7.58	7.62	7.61	7.55	7.65
30	7.44	7.70	7.69	7.70	7.59	7.74
31	7.44	7.50	7.50	7.47	7.53	7.49
32	7.44	7.50	7.50	7.47	7.54	7.50

* Samples are described in Table 2.
‡ CO_2 was lost from flask.

TABLE A-2: SPECIFIC CONDUCTANCE OF CLAY LEACHATES AND SAMPLE BLANKS

	DAYS LEACHED					
Sample	Initial	1	7	21	35	49
1	92.7	102.7	105.3	108.1	108.1	112.2
2	92.7	103.6	106.7	109.1	108.6	109.6
3	92.7	103.3	106.0	108.1	108.6	112.6
4	92.7	103.0	105.0	108.1	108.5	108.5
5	92.7	102.0	106.0	107.3	108.6	113.0
6	92.7	104.3	107.0	108.1	108.6	113.0
7	92.7	104.6	107.0	108.1	108.6	112.6
8	92.7	93.0	95.5	95.1	93.0	96.0
9	95.0	95.7	98.9	101.7	103.3	102.0
10	95.0	95.2	98.6	103.0	104.0	104.3
11	95.0	95.5	97.2	99.2	98.6	98.6
12	95.0	95.2	95.8	95.9	94.6	93.6
13	95.0	104.6	107.0	108.1	108.8	108.8
14	95.0	104.3	106.7	108.5	108.6	108.8
15	95.0	103.3	107.4	108.1	108.5	108.8
16	95.0	104.0	106.4	108.1	108.8	108.8
17	96.0	95.7	97.7	95.8	95.2	94.0
18	96.0	96.3	101.1	104.3	106.7	105.0
19	1.0	34.8	33.8	34.7	34.7	35.5
20	1.0	34.8	34.7	35.5	35.9	36.3
21	1.0	1.3	1.7	1.6	1.6	1.3
22	96.0	97.7	99.8	95.2	95.7	93.3
23	96.0	105.2	107.8	103.6	103.0	101.1
24	96.0	99.9	101.4	96.3	95.8	94.1
25	96.1	167.4	197.9	190.9	178.4	171.8
26	96.1	173.7	206.6	200.3	184.5	177.4
27	96.1	105.7	100.8	105.0	102.3	102.7
28	96.1	98.9	96.3	97.8	97.5	96.6
29	96.1	108.8	109.2	110.7	116.6	120.9
30	96.1	108.8	108.8	108.8	109.6	104.6
31	96.1	96.3	94.4	95.7	93.6	96.0
32	96.1	96.0	94.4	----	95.2	93.6

TABLE A-3: DISSOLVED OXYGEN OF CLAY LEACHATES AND SAMPLE BLANKS

Sample	DAYS LEACHED					
	Initial	1	7	21	35	49
1	8.6	8.7	7.9	8.0	8.3	8.6
2	8.6	8.7	8.0	8.1	7.8	8.4
3	8.6	8.6	8.2	8.2	8.2	7.8
4	8.6	8.9	8.1	7.9	8.6	8.2
5	8.6	8.3	7.6	8.2	8.6	9.6
6	8.6	9.1	8.0	8.6	8.5	8.5
7	8.6	9.0	8.0	8.3	8.5	8.5
8	8.6	9.0	8.1	8.2	8.8	8.4
9	7.8	7.7	7.5	11.7	8.7	8.2
10	7.8	7.9	7.3	4.0	8.4	8.4
11	7.8	7.6	6.7	7.8	8.2	8.6
12	7.8	8.6	7.2	7.9	7.9	8.2
13	7.8	9.5	7.8	7.7	8.8	8.2
14	7.8	9.1	8.4	8.4	8.4	8.6
15	7.8	9.3	7.9	8.4	10.5	8.6
16	7.8	8.9	7.9	7.8	7.0	8.5
17	9.1	7.3	6.7	6.4	6.6	6.6
18	9.1	7.7	6.1	10.9	6.8	7.1
19	5.8	7.7	6.6	6.7	4.9	6.8
20	5.8	7.8	6.8	11.2	7.2	7.1
21	5.8	7.3	7.3	8.3	7.5	7.5
22	1.6	1.6	0.7	1.0	0.6	0.7
23	2.5	2.5	2.8	0.8	0.6	1.1
24	4.1	4.1	0.4	1.4	0.5	0.9
25	4.2	4.2	1.6	1.6	1.2	1.3
26	2.3	2.3	1.2	1.5	1.3	1.6
27	4.7	4.7	7.3	2.8	1.2	1.2
28	2.0	2.0	1.2	---	1.3	1.6
29	8.7	10.4	10.7	5.7	10.1	13.2
30	8.7	10.4	10.8	10.2	10.2	13.1
31	8.7	10.3	10.5	10.5	10.7	13.2
32	8.7	10.3	11.3	15.1	10.7	13.2

TABLE A-4: TOTAL CORRECTED RELEASE OF DISSOLVED SOLIDS IN mg PER g OF CLAY

	DAYS LEACHED				
Sample	1	7	21	35	49
1	11.3	12.7	16.9	21.5	24.5
2	12.5	14.4	19.0	22.6	22.0
3	12.3	13.9	18.1	22.8	25.8
4	11.9	12.6	17.9	22.4	20.6
5	10.6	13.5	16.7	22.2	25.6
6	13.5	15.2	18.2	22.9	26.3
7	13.8	15.2	18.2	22.9	25.9
9	0.7	4.0	7.7	11.6	12.8
10	0	3.3	8.4	11.4	14.4
11	0.52	2.7	6.6	7.8	11.2
13	11.4	14.7	17.2	20.6	24.0
14	10.9	14.2	17.5	20.3	23.9
15	9.6	14.8	16.9	19.8	23.6
16	10.5	13.8	17.0	20.4	23.8
18	1.7	11.6	26.3	37.6	39.4
19	42.7	45.2	50.6	54.8	60.3
20	42.6	46.2	51.6	56.4	61.6
22	-3.0	-2.5	-0.8	-0.7	-1.8
23	6.7	8.7	10.8	11.7	12.2
25	83.2	131.7	133.9	130.3	133.2
26	91.5	144.3	148.3	141.8	144.9
27	15.5	11.8	19.2	16.2	19.4
29	15.9	20.2	23.2	30.1	40.4
30	15.9	19.8	20.9	21.1	18.9
31	0.5	0.2	1.7	-3.5	1.8

TABLE A-5: TOTAL CORRECTED RELEASE OF ALKALINITY IN mg OF $CaCO_3$ PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	9.2	11.3	15.2	16.1	25.3
2	12.3	11.6	15.9	17.7	22.3
3	11.5	14.7	17.4	16.2	22.8
4	11.3	13.5	14.9	17.3	21.6
5	12.1	12.0	17.1	14.8	22.2
6	10.9	13.6	16.0	18.3	22.7
7	14.6	15.1	18.0	18.7	25.4
9	-0.4	1.6	----	6.0	9.5
10	-0.2	4.8	7.9	9.4	10.2
11	2.1	9.9	5.7	4.7	11.2
13	7.7	9.2	14.8	15.5	20.0
14	6.7	8.5	13.0	15.8	19.9
15	7.8	11.8	13.7	16.1	21.4
16	8.2	11.4	14.4	13.1	19.5
18	0.5	6.0	20.6	28.7	34.8
19	31.6	31.9	28.9	43.7	49.7
20	34.1	34.5	25.0	45.9	52.0
22	-2.2	-2.6	-2.4	-0.4	2.2
23	7.6	11.4	11.3	10.1	14.0
25	80.2	127.1	119.0	111.6	134.7
26	78.5	127.0	140.1	136.3	144.3
27	19.3	20.4	8.5	21.1	26.5
29	15.7	20.7	22.3	29.0	40.3
30	13.4	19.7	24.2	24.6	26.7
31	-1.1	-3.3	1.5	4.5	2.9

TABLE A-6: TOTAL CORRECTED RELEASE OF ORTHOPHOSPHATE IN μg OF PO_4 PER g OF CLAY

	DAYS LEACHED				
Sample	1	7	21	35	49
1	19	21	13	22	14
2	32	21	21	26	23
3	23	26	11	10	6
4	21	21	14	19	13
5	38	36	39	40	24
6	42	36	35	45	9
7	32	24	23	28	9
9	25	39	73	81	63
10	24	45	71	76	89
11	0	30	41	47	36
13	19	15	23	15	43
14	15	11	12	13	22
15	26	6	24	24	37
16	28	9	23	20	28
18	43	153	133	185	132
19	51	26	47	54	44
20	62	41	55	40	41
22	4	25	5	36	63
23	27	45	14	6	29
25	63	49	50	77	70
26	71	38	43	60	56
27	74	69	78	75	80
29	15	29	26	26	32
30	15	46	28	33	32
31	11	34	27	26	28

TABLE A-7: TOTAL CORRECTED RELEASE OF TOTAL SOLUBLE P IN µg OF P PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	2	4	18	3	59
2	12	3	22	9	64
3	2	8	-0.5	11	3
4	4	5	20	5	20
5	9	7	33	12	43
6	15	10	30	14	31
7	9	4	22	6	31
9	9	20	18	22	25
10	8	12	19	22	23
11	0	4	3	17	21
13	9	8	10	1	5
14	6	2	--	3	10
15	12	--	8	7	7
16	13	5	5	5	13
18	49	74	70	65	42
19	38	37	24	14	14
20	9	43	10	29	12
22	11	--	--	19	14
23	8	--	5	7	4
25	7	44	24	25	24
26	27	26	31	24	4
27	33	50	45	30	28
29	17	23	25	14	14
30	12	34	10	14	10
31	11	13	10	11	7

TABLE A-8: TOTAL CORRECTED RELEASE OF NITRATE IN mg PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	0.09	0.11	0.01	0.05	0.08
2	0.12	0.19	0.11	0.07	0.20
3	0.08	0.09	-0.05	-0.01	0.03
4	0.05	0.04	0.01	-0.02	0.07
5	-0.06	0.05	-0.14	-0.03	0.24
6	-0.02	0.02	-0.02	-0.03	-0.21
7	-0.04	0.00	-0.11	-0.03	0.01
9	0.18	0.25	-0.16	0.36	0.17
10	0.15	0.20	-0.13	0.48	0.47
11	0.11	0.16	0.04	0.36	0.51
13	0.14	0.06	0.09	0.00	-0.10
14	-0.02	-0.04	-0.03	0.03	-0.09
15	0.01	0.03	0.04	0.03	-0.17
16	-0.02	-0.08	-0.06	0.05	0.12
18	0.05	0.56	2.45	2.90	3.09
19	0.16	0.07	0.10	0.09	0.13
20	0.22	0.12	0.11	0.08	0.12
22	-0.10	-0.21	-0.10	-0.30	-0.43
23	-0.12	-0.23	-0.47	-0.73	-0.98
25	0.26	-0.05	-0.15	0.06	0.12
26	0.10	0.01	0.10	-0.06	0.18
27	0.26	-0.34	-0.24	0.01	0.02
29	-0.22	0.15	-0.32	0.56	0.18
30	0.02	0.14	0.08	0.23	0.10
31	-0.24	-0.27	-0.54	-0.49	0.04

TABLE A-9: TOTAL CORRECTED RELEASE OF CHLORIDE IN mg PER g OF CLAY

	DAYS LEACHED				
Sample	1	7	21	35	49
1	0.98	0.35	2.47	1.68	1.83
2	0.57	0.10	0.68	0.31	-0.23
3	0.42	0.24	0.50	0.29	0.06
4	0.32	-0.21	-0.04	-0.46	0.47
5	0.36	-0.12	0.16	-0.36	0.02
6	0.25	-0.18	0.10	-0.18	-0.18
7	0.00	-0.22	-0.13	-0.32	-0.05
9	-0.03	0.53	0.22	-1.07	-0.31
10	-0.58	0.25	-0.90	-0.47	-0.24
11	-1.27	1.52	0.45	-0.29	-0.09
13	-0.66	1.28	-0.51	-0.50	-0.05
14	-0.36	0.84	-0.74	-0.72	-0.18
15	-0.30	0.24	-0.74	-1.41	-0.54
16	-0.26	1.71	-1.08	-1.15	-0.38
18	0.80	0.37	0.39	-0.44	0.37
19	0.03	0.33	0.06	0.07	-0.27
20	0.08	-0.03	0.03	-0.05	-0.66
22	0.01	0.13	0.72	-0.13	-0.20
23	-0.21	-0.10	0.66	-0.19	-0.12
25	0.31	-0.11	-0.00	-0.16	-0.09
26	0.11	-0.05	-0.11	-0.02	-0.06
27	0.46	0.08	0.18	0.23	-0.15
29	-0.07	0.29	0.03	-0.01	-0.06
30	-0.11	0.39	-0.03	0.03	-0.22
31	-0.12	-0.06	-0.42	0.02	-0.14

TABLE A-10: TOTAL CORRECTED RELEASE OF TOTAL KJELDAHL N IN mg OF N PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	0.16	-0.14	0.36	0.05	-0.04
2	0.21	-0.12	0.13	-0.06	-0.03
3	0.18	-0.09	0.25	-0.12	-0.04
4	0.09	0.15	0.15	-0.13	-0.09
5	0.09	0.02	-0.07	-0.04	0.13
6	0.06	0.02	-0.12	-0.10	-0.05
7	0.04	-0.04	-0.14	0.05	0.00
9	0.07	0.01	-1.07	0.02	--
10	0.02	-0.03	-0.63	-0.21	--
11	-0.05	-0.06	-1.27	-0.08	--
13	0.07	-0.03	-0.58	-0.14	--
14	0.04	-0.09	0.13	-0.21	--
15	0.00	-0.10	-0.05	-0.27	--
16	0.03	-0.08	-0.16	-0.39	--
18	-0.11	0.40	-0.23	0.02	0.48
19	-0.23	0.14	0.03	0.19	--
20	-0.27	0.26	-0.08	-0.04	--
22	-0.21	-0.01	0.14	0.10	--
23	-0.14	-0.04	-0.01	-0.23	--
25	0.06	0.02	0.01	0.13	0.18
26	0.00	0.01	0.06	-0.21	0.09
27	0.00	0.24	0.21	-0.20	0.24
29	-0.04	-0.08	0.04	-0.47	0.16
30	-0.08	-0.19	-0.01	-0.45	-0.18
31	-0.07	-0.16	-0.02	-0.72	-0.30

TABLE A-11: TOTAL CORRECTED RELEASE OF SODIUM IN mg PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	0.39	0.56	-0.20	2.04	1.62
2	0.19	0.45	-0.09	0.53	0.25
3	0.24	0.06	-0.51	0.65	-0.12
4	0.08	-0.05	-0.63	-0.69	-0.01
5	0.18	0.19	0.91	-0.07	0.28
6	0.37	1.93	--	-0.61	-0.34
7	0.24	0.08	--	0.15	-0.10
9	0.39	0.12	1.88	1.11	0.91
10	0.09	-0.08	0.16	0.13	1.32
11	0.12	4.50	3.33	0.00	0.69
13	0.30	0.15	1.02	-0.18	0.32
14	0.08	0.19	1.14	0.97	0.55
15	0.20	0.18	3.15	0.17	0.27
16	0.06	0.43	1.96	0.30	0.38
18	0.19	2.72	4.49	-0.59	0.10
19	0.21	0.44	0.74	0.76	0.74
20	0.06	1.54	0.45	0.69	0.74
22	-0.14	0.20	0.15	0.07	0.54
23	0.10	0.18	-0.06	-0.58	0.79
25	0.54	2.38	1.05	0.30	0.16
26	0.28	0.11	0.18	-0.17	-0.21
27	-0.04	-0.54	-0.06	0.10	0.46
29	0.49	0.93	0.17	0.41	0.35
30	0.45	0.68	1.47	0.39	0.32
31	0.51	0.11	0.42	0.20	0.18

TABLE A-12: TOTAL CORRECTED RELEASE OF POTASSIUM IN mg PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	0.37	0.25	0.06	-0.04	0.48
2	0.39	0.15	0.06	0.02	0.21
3	0.36	0.35	0.01	-0.18	0.34
4	0.45	0.34	0.08	-0.04	0.42
5	0.47	0.38	0.12	0.24	0.55
6	0.41	0.38	0.11	0.04	0.63
7	0.45	0.34	0.15	--	0.31
9	0.06	0.07	0.24	0.63	0.33
10	0.00	0.13	0.26	0.51	0.28
11	0.12	0.14	-0.01	0.27	0.12
13	0.26	0.26	0.17	0.48	0.15
14	0.22	0.36	0.13	0.40	0.18
15	0.35	0.41	0.23	0.77	0.14
16	0.48	0.45	0.32	0.79	0.16
18	0.24	0.16	0.19	0.35	0.24
19	0.40	0.31	0.36	0.45	0.39
20	0.40	0.44	0.42	0.55	0.51
22	0.20	0.32	-0.11	0.22	0.24
23	0.29	0.05	-0.18	0.15	0.11
25	0.34	0.58	0.43	0.34	0.35
26	0.30	0.31	0.38	0.31	0.38
27	0.15	0.21	0.26	0.40	0.40
29	0.16	0.22	0.28	0.31	0.28
30	0.14	0.47	0.37	0.34	0.88
31	0.03	0.31	0.26	0.15	0.21

TABLE A-13: TOTAL CORRECTED RELEASE OF CALCIUM IN mg PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	1.17	1.86	0.10	--	4.82
2	0.97	2.43	0.14	--	5.31
3	2.18	3.43	0.42	-1.96	6.72
4	2.37	2.81	1.29	7.10	6.76
5	1.37	3.84	2.46	10.85	8.54
6	1.97	4.33	2.19	9.04	6.32
7	0.59	3.60	1.99	7.85	4.45
9	-0.41	0.78	-0.16	1.46	-0.86
10	-0.19	0.54	1.16	4.27	2.25
11	0.31	0.95	1.66	-1.88	-3.02
13	2.78	3.86	0.83	4.23	7.59
14	2.58	3.63	2.97	3.81	3.11
15	2.16	3.16	2.28	1.67	3.14
16	0.99	2.87	1.17	3.03	1.70
18	0.00	2.41	5.55	-1.16	1.59
19	10.52	13.05	14.88	16.35	16.37
20	10.30	12.59	15.00	14.81	15.95
22	-0.70	-2.63	-3.12	-3.16	-0.84
23	2.30	0.65	0.06	0.88	2.64
25	18.07	28.11	26.32	27.71	24.22
26	22.47	32.81	31.62	27.16	28.26
27	7.60	4.94	5.36	6.92	3.65
29	3.70	4.44	4.87	5.71	9.06
30	2.68	4.14	3.73	4.47	4.63
31	0.28	-0.31	-1.99	-2.06	-0.98

TABLE A-14: TOTAL CORRECTED RELEASE OF MAGNESIUM IN mg PER g OF CLAY

Sample	DAYS LEACHED				
	1	7	21	35	49
1	1.18	1.03	1.24	1.50	1.25
2	1.22	1.11	1.33	1.89	1.27
3	0.79	0.63	0.89	1.26	0.87
4	0.91	0.66	1.06	0.91	0.90
5	-0.02	0.13	0.40	0.54	0.35
6	0.24	0.07	0.61	0.53	0.46
7	1.26	1.37	1.12	1.89	1.32
9	0.02	0.48	1.08	1.04	1.72
10	0.13	0.35	1.21	1.19	1.77
11	0.28	0.27	1.13	1.24	2.18
13	0.78	0.73	0.96	0.66	1.14
14	0.63	0.80	0.89	0.37	0.94
15	1.18	1.28	1.35	1.07	1.22
16	1.13	1.26	1.44	1.24	1.19
18	0.34	0.90	1.47	1.70	1.37
19	2.53	2.59	2.70	3.02	3.46
20	2.44	2.51	2.57	2.99	3.43
22	0.02	-0.18	-0.18	-0.03	-0.27
23	0.94	0.83	0.69	1.06	0.51
25	2.13	2.08	2.39	2.29	2.59
26	2.21	2.10	2.45	2.36	2.71
27	1.37	1.20	1.31	2.06	1.47
29	1.01	1.11	0.92	0.34	1.10
30	0.95	1.15	0.98	0.44	0.97
31	0.17	0.30	0.27	-0.33	0.51

APPENDIX B

U.S. EPA - University of Wisconsin
Analytical Quality Control Results
and Their Impact on the
Chemical Loading Estimates

INTRALAB COMPARISONS

An analytical quality control (AQC) program was carried out during the course of the study. This program consisted of University of Wisconsin, Superior (UWS) analysis of reference samples provided by the EPA and analysis of split samples by both laboratories. The split samples were chosen at random from those analyzed by the University of Wisconsin and generally consisted of Lake Superior water samples which had been obtained during the leaching and exchange studies or from the Lake Superior water-sampling phase.

The results of the AQC comparisons are shown in Table B-1 according to the parameters analyzed. Those samples which do not have UWS sample numbers are reference samples provided by the EPA Region V Laboratories, Chicago, Illinois (CRL) while those which do have UWS sample numbers are the split-water samples.

The comparisons shown in Table B-1 were tested for significant differences between the results of the two laboratories for those samples which were compatible with a statistical analysis. The null hypothesis assuming the two "means" for a particular analysis are identical at a 95% probability level was used by employing the expression.[13]

$$t = \frac{|\bar{X}_1 - \bar{X}_2|}{S} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

where $\bar{X}_1$ and $\bar{X}_2$ are the two means in question, S is the standard deviation in the determination of the means (assuming it is the same for both laboratories), and n_1 and n_2 are the number of individual results obtained by the two laboratories in determining the mean values. The t value determined is compared to tabulated values according to the degrees of freedom ($n_1 + n_2 - 2$) at the desired probability level. If the t value computed is less than the tabulated t value at the appropriate probability level (95% is used here), then the two means are identical within the level tested.

Each analysis was not performed in multiplate due to time, budget, and manpower limitations and thus standard deviations are not available for each individual determination. During the course of this study, many of the analytical determinations of each parameter were performed in duplicate, and these replicate determinations have been used to establish average standard deviation values for the UWS analysis of these parameters. Standard deviations were calculated for the analysis of samples having parameter values of the same magnitude as those used in the loading to Lake Superior calculations. The average standard-deviation values for a large number of repli-

TABLE B-1: SUMMARY OF E.P.A.-UNIVERSITY OF WISCONSIN AQC PROGRAM

All concentrations are in mg/l.

Date 1975	Sample No. UW-S	Sample No. CRL	Orthophosphate-P UW-S	Orthophosphate-P CRL	Date 1975	Sample No. UW-S	Sample No. CRL	Total Soluble-P UW-S	Total Soluble-P CRL
6/4	--	Nutrient Ref Conc 1	0.024	0.021	4/25	--	ULRG#5 #43	1.37	1.46
6/4	--	Nutrient Ref Conc 2	0.395	0.393	4/25	--	ULRG#5 #44	1.65	1.69
5/30	1	10755	0.033	<0.007	4/25	--	ULRG#5 #45	0.128	0.18
6/7	357	10771	0.001	<0.007	4/25	--	ULRG#5 #46	0.149	0.17
6/7	323	10773	0.001	<0.007	6/4	--	Nutrient Ref Conc 3	0.093	0.142
6/25	13	11001	0.018	<0.007	6/4	--	Nutrient Ref Conc 4	0.767	0.713
7/7	L.W.	8209	0.001	<0.007	5/30	2	10756	0.012	0.010
7/23	9	8221	0.031	<0.007	6/7	357	10771	0.003	<0.007
7/23	13	8222	0.020	<0.007	6/7	323	10773	0.005	<0.007
					6/25	13	11001	0.003	<0.007
					7/7	L.W.	8209	<0.001	<0.007
					7/23	9	8221	0.014	<0.007
					7/23	13	8222	0.014	<0.007

Continued

TABLE B-1 (continued)

Date 1975	Sample No. UW-S	Sample No. CRL	TKN UW-S	TKN CRL	Date 1975	Sample No. UW-S	Sample No. CRL	Nitrate UW-S	Nitrate CRL
4/25	--	ULRG#5 #43	3.40	4.03	6/4	--	Nutrient Ref Conc 1	0.368	0.20
4/25	--	ULRG#5 #44	3.87	4.85	6/4	--	Nutrient Ref Conc 2	1.170	1.11
4/25	--	ULRG#5 #45	5.30	6.51	5/30	4	10758	0.22*	0.31
4/25	--	ULRG#5 #46	4.62	5.85	6/7	337	10776	0.22*	0.28
6/4	--	Nutrient Ref Conc 3	0.102	0.35	6/7	317	10777	0.23*	0.28
6/4	--	Nutrient Ref Conc 4	0.332*	5.80	6/25	14	11007	0.25*	0.28
5/30	3	10757	0.0	0.21	7/7	L.W.	8213	0.24*	0.28
6/7	317	10773	0.06	0.28	7/23	15	8226	0.20*	0.28
6/7	320	10780	0.25*	0.69	7/23	11	8227	0.22*	0.28
6/25	11	11003	0.01	0.27	8/6	9	8240	0.24*	0.27
6/25	12	11004	0.04	0.31	8/6	14	8241	0.26	0.26
6/25	L.W.	11005	0.02	0.25	8/15	2	8249	0.32*	0.39
7/7	L.W.	8211	0.04	0.11	8/15	13	8250	0.23*	0.29
7/7	8	8212	<0.01	0.08	8/15	15	8251	0.23*	0.31
7/23	10	8224	0.033	0.12	8/15	16	8252	0.21*	0.31
7/23	14	8225	0.063	0.08	8/15	316	8253	0.19*	0.22
8/6	13	8242	0.03	0.10	8/15	320	8255	0.20*	0.29
8/6	15	8243	<0.01	0.10	8/15	349	8257	0.18*	0.21
8/15	2	8249	0.22	0.16					
8/15	13	8250	0.39	0.12					
8/15	15	8251	0.21	0.11					
8/15	16	8252	0.28	0.12					
8/15	316	8254	0.18	0.05					
8/15	320	8256	0.18	0.07					
8/15	349	8258	0.24	0.09					

* Differences between laboratories are statistically significant.

Continued

TABLE B-1 (continued)

Date	Sample No.		Silica		Date	Sample No.		Chloride	
1975	UW-S	CRL	UW-S	CRL	1975	UW-S	CRL	UW-S	CRL
4/30	--	ULRG#6 #51	2.4	2.3	4/30	--	ULRG#6 #51	1.1	1.2
4/30	--	ULRG#6 #52	2.3	2.2	4/30	--	ULRG#6 #52	1.7	1.8
4/30	--	ULRG#6 #53	1.2	1.1	4/30	--	ULRG#6 #53	5.3	5.3
4/30	--	ULRG#6 #54	1.0	1.0	4/30	--	ULRG#6 #54	4.8	4.8
4/30	--	ULRG#6 #55	0.2	0.2	4/30	--	ULRG#6 #55	7.4	7.4
4/30	--	ULRG#6 #56	0.3	0.2	4/30	--	ULRG#6 #56	8.5	8.2
6/7	362	10783	3.24	2.89	5/30	5	10760	1.59	1.6
6/7	320	10784	3.15	2.98	6/7	362	10783	1.70	1.6
6/25	3	11009	3.7*	4.63	6/7	320	10784	3.42*	3.2
6/25	10	11010	2.8	2.6	6/25	16	11008	1.45	1.4
6/25	17	11011	2.7	2.8	7/7	L.W.	8215	1.09	1.2
7/7	1	8216	4.97	4.63	7/23	13	8229	1.19	1.3
7/7	5	8217	2.84	2.51	7/23	16	8230	1.19	1.3
7/7	14	8218	4.60	4.02					
7/23	9	8231	5.6*	4.78					
7/23	10	8232	3.0	2.71					
7/23	16	8233	3.0	2.70					
8/6	5	8245	2.90	2.65					
8/6	10	8246	2.80*	0.36					
8/6	15	8247	4.80	4.17					
8/15	319	8260	2.52	2.33					
8/15	341	8261	2.81	2.54					
8/15	362	8262	2.70	2.50					

* Differences between laboratories are statistically significant.

Continued

TABLE B-1 (continued)

Date	Sample No.		Calcium		Magnesium		Potassium		Sodium	
1975	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL
5/30	6	10761	15.0	15.1	3.10*	3.3				
5/30	7	10761					0.63	0.65	2.11*	1.0
6/7	341	10790	11.9	12.8	3.28*	2.99	0.67	0.60	2.90*	1.55
6/7	1	10791	12.2*	15.1	3.33	3.25	0.73*	0.63	3.07*	1.41
6/7	316	10792	12.8	12.9	3.04	3.00	0.60	0.58	2.30*	1.53
6/7	320	10794								
6/7	362	10795								
6/25	9	11012	14.5	14.9	3.46	3.5	0.72	0.66	1.86*	1.7
7/7	L.W.	8219	14.6*	11.6	3.36*	2.8	0.42*	0.52	1.13*	1.48
7/23	12	8234	14.3*	11.8	3.4*	2.8	0.52	0.59	1.20*	1.63
7/23	13	8235	15.6*	13.7	3.7*	3.3	0.66	0.68	1.05*	1.34
8/4	7	8243								
8/4	8	8244								
8/4	9	8245								
8/6	10	8237	23.9*	26 9	4.19*	5.8	0.72*	0.64	1.46*	1.3
8/6	16	8238	13.4	13.0	3.36*	3.0	0.60*	0.51	1.48	1.4
8/15	142	8272	14.0	12.8	3.35*	3.0	0.59*	0.48	1.73*	1.4
8/15	337	8273	13.4	13.2	3.27*	3.1	0.57	0.51	1.62*	1.4

* Differences between laboratories are statistically significant.

Continued

TABLE B-1 (continued)

Date	Sample No.		Copper		Iron		Lead		Manganese	
1975	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL
4/16	--	10601	7	8	28	20	<1	1	1.4	1.4
4/16	--	10602	4	4	20	10	<1	<1	0.8	1.0
4/16	--	10603	7*	3	20	<10	<1	<1	1.0	1.4
4/16	--	10604	8*	4	32	<10	<1	<1	1.4	1.2
6/7	337	10785			1097	810				
6/7	349	10786			803	570				
6/7	349	10787			54	70				
6/7	347	10788			69	90				
6/7	320	10794	5	7					8.3	8.5
6/7	362	10795	5	4					2.6	2.5
8/4	7	8243	1.8	3	30	44	<1	<1	1.5	1.0
8/4	8	8244	4	4	260	300	2	1	10.0*	5.8
8/4	9	8245	4	4	62	70	<1	<1	4.2*	10
8/15	1	8264	2.5	2.0	13	<5			3.0*	1.1
8/15	2	8265	2.7	2.5	4770	4600			3760	4900
8/15	3	8266	4.0	2.5	3950	2900			4770	2900
8/15	4	8267	3.5	2.0	11	<5			5.8*	3.5
8/15	317	8268	3.5	1.5			<1	<2	8.0*	3.5
8/15	343	8269	1.3	0.5			<1	<2	2.3	1.0
8/15	357	8270	2.3	1.0			<1	<2	3.0*	1.2

* Differences between laboratories are statistically significant.

Continued

TABLE B-1 (continued)

Date	Sample No.		Nickel		Zinc		Cadmium		Chromium		Aluminum	
1975	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL	UW-S	CRL
4/16	--	10601	<20	<20	12	11	1.0	0.8	0.8	<1		
4/16	--	10602	<20	<20	7	7	0.2	<0.2	1.3	<1		
4/16	--	10603	<20	<20	6	5	0.2	<0.2	0.3	<1		
4/16	--	10604	<20	<20	6	5	0.2	<0.2	0.3	<1		
6/7	337	10785										
6/7	349	10786										
6/7	349	10787										
6/7	347	10788										
6/7	320	10794			7.0	6.0	0.3	0.4				
6/7	362	10795			7.9	13.0	1.3	1.3				
8/4	7	8243			2	<5	<0.1	<0.1			--	10
8/4	8	8244			6	<5	<0.1	<0.1			--	130
8/4	9	8245			13	<5	<0.1	<0.1			67	85
8/15	1	8264			7.4	<5	0.09	0.10				
8/15	2	8265			8.0	<5	0.01*	2.2				
8/15	3	8266			6.4	14	0.03*	0.7				
8/15	4	8267			5.0	<5	0.05	<0.1				
8/15	317	8268			6.1	<5	0.05	<0.1				
8/15	343	8269			0.9	<5	0.02	<0.1				
8/15	357	8270			2.4	<5	0.05	<0.1				

* Differences between laboratories are statistically significant.

cates are listed in Table B-2, together with the range of concentration of the parameter in those samples which were used in the calculations.

In the calculation of the t values, it is assumed that the standard deviation values for the two laboratories are the same as listed in Table B-2. The values for n_1 and n_2 are taken as two since at most two determinations were made on the individual analysis of a particular parameter and the same situation is assumed to exist for the EPA results. Consequently, the expression for the t values reduces to:

$$t = \frac{\left| X_1 - X_2 \right|}{S}$$

and these computed values are compared to a Student's t value of 4.3 for two degrees of freedom.[13]

This test for significant differences in the analytical determinations of the parameters does not indicate which results are the more correct results but will indicate potential systematic errors in their determinations. This information coupled with the degree of agreement between the two laboratories will assist in the estimates of uncertainties in the loadings for the various parameters.

Those individual determinations in which there are significant differences between the data of the two laboratories are indicated by asterisks assigned to the UWS values in Table B-1. The results show that there are significant differences occurring for some of the parameters, but for others the agreement is within those limits predicted by assuming only random fluctuations in the data. It should be stressed that there is up to a three-month time difference in the analysis of the split samples between the two laboratories.

The comparisons for orthophosphate -P and total soluble phosphorus are limited because of sample stability and the low values of these parameters in the lake-water samples. The only valid comparisons for orthophosphate pertain to the results for nutrient reference samples in which the values are in good agreement. For total soluble phosphorus, the reference samples were too concentrated for comparisons at the levels at which standard deviations were established. However, comparisons of those reference samples appear to be fairly good. Only one sample (CRL-10756) was statistically tested and there is no significant difference between the values.

All total Kjeldahl nitrogen values were tested statistically except for the high-concentration samples (CRL #43, #44, #45, #46). There are significant differences in two of the comparison values, with one being extremely large. The standard deviation for total Kjeldahl nitrogen for the University of Wisconsin determinations is relatively large (0.067 mg/l), and consequently the statistical test would indicate no significant differences at the low-concentration levels found in the soil and sediment-leaching samples in Lake Superior water. UWS replicate results indicate that there is a

TABLE B-2: UNIVERSITY OF WISCONSIN AVERAGE STANDARD-DEVIATIONS FOR REPLICATE ANALYSIS

Parameter	Average Standard Deviation*	Concentration Range
Orthophosphate -P	0.0020	0.005 - 0.034 mg/1
Total Soluble Phosphorus	0.0015	0.006 - 0.017 mg/1
Alkalinity	0.38	20 - 50 mg/1
Specific Conductance	0.44	92 - 272 µmhos
pH	0.02	7.5 - 8.3
Calcium	0.26	12 - 17 mg/1
Magnesium	0.036	3.3 - 4.3 mg/1
Sodium	0.0325	0.3 - 3.7 mg/1
Potassium	0.017	0.5 - 1.0 mg/1
Chloride	0.031	1.0 - 4.6 mg/1
Nitrate - NO_3	0.005	0.8 - 1.3 mg/1
Kjeldahl -N	0.067	0.03 - 0.4 mg/1
Silica (SiO_2)	0.17	2.6 - 3.2 mg/1
Aluminum	7.1	50 - 100 µg/1
Copper	0.76	1 - 10 µg/1
Cadmium	0.03	0.15 - 1.25 µg/1
Manganese	0.36	1 - 10 µg/1
Zinc	2.5	1 - 14 µg/1
Iron	15	30 - 150 µg/1

* The units are the same as those listed under the concentration range.

significant degree of uncertainty in the UWS values. Therefore, the EPA results were heavily relied upon as a basis for the conclusions regarding total Kjeldahl nitrogen inputs (summarized in Section 9).

The statistical testing of the nitrate -N values for the water samples showed that nearly all the values were significantly different. This is a direct result of the small standard deviation in replicate determinations for the University of Wisconsin analysis (0.005 mg/l), as any difference greater than 0.02 mg/l between the two laboratories is significant. All of the University of Wisconsin values for the water samples are lower (except for the one value in which there was agreement) by an average of 0.06 mg N per liter or approximately 20% of the value determined. However, since there is good internal agreement within the UWS data, and the concentrations of NO_3 in the samples and Lake Superior water blanks have similar values, the procedure of subtracting the apparent release in a lake-water blank from the apparent release in the sample should largely cancel out a possible systematic error in both values. For example, if both the sample and lake-water blank values for nitrate were low by 0.06 mg/l, the correct difference in the samples would be obtained in the subtraction process. Consequently, the statistical comparison analysis would indicate the release values should be valid within reasonably small uncertainties, even though there are differences on the order of 20% in the determinations by the two laboratories.

The statistical comparisons of the silica data show only three significant differences out of 19 samples tested. There was an obvious mistake in one sample (CRL-8246), as this was listed as being a Lake Superior water sample and could not possibly contain 0.36 mg/l of SiO_2. Consequently, this comparison was disregarded. The overall agreement with respect to silica is reasonably good.

The agreement for chloride is very good, with only one sample showing a significant difference, and the difference for this sample is only 0.22 mg/l out of 3.4 mg/l.

The statistical tests for calcium showed that five of the twelve comparisons were significantly different. The University of Wisconsin values were generally higher than the EPA results. Similarly, five out of twelve potassium values and nine out of twelve comparisons for magnesium were significantly different. However, the standard deviations for UWS determinations of potassium and magnesium are small (0.016 and 0.036 mg/l respectively), and the actual agreement for most of the samples was reasonably good.

A larger uncertainty exists in the sodium determinations. Only one of the twelve values compared showed statistical agreement. The first four listed values showed extremely large discrepancies in the values from the two labs. These particular values were not used in any of the loading calculations, as these determinations were made in the earlier phase of the analytical work before the leaching experiments were begun. The latter values show better agreement, but significant differences remain. The standard deviation in the UWS replicate analysis is small (0.14 mg/l) compared to the differences in the results between the two labs. These differences will be considered in the loading estimate uncertainties.

There are no significant differences in the aluminum, iron, and zinc values, although there is only one comparison for aluminum and the standard deviations for zinc and aluminum are higher than those for most of the other trace metals. Copper, lead, and cadmium agreements are good as is the agreement for manganese at lower concentration levels. The data is insufficient to allow comparisons on nickel and chromium.

PROJECTION OF AQC PROGRAM TO LOADING UNCERTAINTIES

The results of the AQC program should provide a basis for the estimation of uncertainties in the chemical-loading parameters. Average standard deviations for the EPA-UWS comparison values (Table B-1) were calculated for the data pairs corresponding to the same concentration ranges as used in the loading estimates. These computed values are listed in Table B-3.

The projection of the AQC program to loading uncertainties was accomplished by considering the AQC standard deviations in the mathematical expressions used for calculating the chemical releases.

The chemical releases determined by the seven-week leaching studies (Section 4) were computed by an expression of the form

$$R = \frac{10X_n - 10X^1 + 5X_i}{5}$$

where X_n, X^1 and X_i are concentrations in mg/l or ug/l and the denominator (5) represents the approximate dry weight of the soil or sediment sample in grams. The coefficient 5 for X_i represents the five one-liter additions of lake water during the seven-week experiments. Since the X values represent water concentrations in the same concentration range, they are all assumed to have uncertainties S_1 represented by the data listed in Table B-2. S_R, the standard deviation in the result R (mg of leached parameter per gram of soil or sediment) is given by the square root of the sum of the standard deviations in the three terms used to calulate R:

$$S_R = \left[(2S_1)^2 + (2S_1)^2 + (S_1)^2\right]^{1/2}$$

This expression reduces to:

$$S_R = 3S_1$$

The standard deviations computed using this expression are listed in Table B-3 according to parameter under the heading "Standard Deviations in Soil or Sediment Releases."

For the leaching of river particulates, approximately two grams of particulate matter (dry weight) was used per 10 liters of lake water. Consequently, the uncertainty in the particulate releases due to the uncertainties indicated by the AQC comparisons is calculated by considering the expression

$$R = \frac{10X_n - 10X^1 + 5X_i}{2}$$

and S_R is given by

$$S_R = 7.5\ S_1$$

These standard deviations are also listed in Table B-3 under the heading "Standard Deviations in Particulate Releases."

The standard deviations in the interstitial water concentrations are the same as those listed for the "Average Standard Deviations" in Table B-3, since only one value for each parameter is used in the loading calculations. However, the magnitudes of the parameters in the interstitial waters varied substantially in some cases from their magnitudes in lake water and thus the standard deviations in Table B-3 would not directly apply to the concentrations of these parameters without a correction for these differences.

The chemical inputs of trace metals due to soil erosion and leaching of resuspended sediments has been listed in Table 20 and summarized in Section 9. The releases in this case are computed from data obtained on changes in metal concentrations in 500 ml of a water sample containing approximately one gram of solid sample. The expression for the release is of the form

$$R = \frac{0.5\ X_1 - 0.5\ X_o}{1}$$

where X_1 and X_o are final and initial concentrations of the metal respectively. Thus, the standard deviation in R is given by

$$S_R = \left[(0.5\ S_1)^2 + 0.5\ (S_1)^2\right]^{\frac{1}{2}} = 0.71\ S_1$$

where it has been assumed that the standard deviation in X_1 and X_o are the same. These standard deviation values for the releases of cadmium, copper, iron, manganese, and zinc are listed in Table B-3 under the heading "Standard Deviations in Soil or Sediment Releases".

The values listed in Table B-3 were used to estimate the magnitude of uncertainty in the estimates of the chemical inputs to Lake Superior summarized in Section 9.

TABLE B-3: INTERLABORATORY COMPARISONS AND LOADING UNCERTAINTIES

Parameter	Average Standard Deviation (mg/1)	Standard Deviations in Soil or Sediment Releases (mg/g)	Standard Deviations in Particulate Releases (mg/g)
Orthophosphate $-PO_4$	0.0054	0.015	0.040
Total Soluble P	0.035	---	0.26
Nitrate $-NO_3$	0.15	0.45	1.1
Silica $-SO_2$	0.26	0.78	---
Chloride	0.072	0.21	0.54
Calcium	0.87	2.6	6.5
Magnesium	0.20	0.6	1.5
Potassium	0.047	0.14	0.35
Sodium	0.18	0.56	1.3
Cadmium	0.000055	0.00004	
Copper	0.00093	0.0007	
Iron[1]	0.010	0.007	
Manganese	0.0012	0.008	
Zinc	0.0017	0.0012	

[1]Computed for a 0.038 to 0.148 mg/1 comparison range.

APPENDIX C

Methods of Analyses For

Sediments and Water Samples

A. Sediment Cores

The data for the sediment core analyses was presented in Tables 11 and 12. The specific methods for the analysis of each parameter are described below:

1. pH. The pH of the sediments was measured by insertion of glass and silver-silver chloride electrodes one centimeter below the sediment surfaces and employing a Corning Model 5 pH meter.

2. Eh. Eh values were obtained by insertion of a platinum and saturated calomel electrode into the sediment at various depths and reading the millivolt display on a Corning Model 5 pH meter upon obtaining steady readings.

3. Total Solids. Tared sediment sub-samples were dried overnight at 103 to 105°C and measured for weight loss.

4. Chemical Oxygen Demand. To a weighed portion of the sample, distilled water and sulfuric acid were added for preservation. The samples were refluxed in potassium dichromate and the unreacted dichromate was titrated with standard ferrous ammonium sulfate. The volume of titrant used for the sample was corrected for dichromate loss utilizating blanks carried through the same digestion and titration procedure.[14]

5. Total Phosphorus. The samples were digested using a mixture of nitric and perchloric acids. The resulting orthophosphate was then determined colorimetrically using the stannous chloride method.[11]

6. Total Iron. Ten-gram samples were brought into solution with HNO_3, H_2O_2 and $NaNO_3$. They were evaporated to dryness and ashed in a muffle furnace at 550°C. The residues were redissolved in 1:1 HCl and filtered into 100 ml volumetric flasks. The samples were made alkaline and the ferric ion reduced to ferrous ion with hydroxylamine hydrochloride. Acetate buffer and phenanthroline were added. After dilution of each sample to 100 ml, absorbance measurements were made at 510 nm. The resulting absorbance values were compared to values for known iron solutions in order to quantitate the results.[14]

7. Kjeldahl Nitrogen. The sediment sample was digested for 30 minutes in a H_2SO_4, Na_2SO_4, and $HgSO_4$ aqueous solution. The solution was cooled, water was added, followed by addition of a 50% $NaOH$-$Na_2S_2O_3$ solution. The resulting solution was distilled, using a 2% boric acid solution to collect the distillate. The collected distillate was titrated with standard H_2SO_4. The results for the samples were corrected by running blanks through the same procedure.[14]

8. Particle-Size Analysis. The pipet-sedimentation method was used in which the sample is dispersed through a #230 mesh sieve into a cylinder containing distilled water and Calgon. Aliquots of the suspension are collected by pipet at a distance 10 cm below the surface as a function of time. The weights of particles in the aliquots are determined by drying the aliquots at 105°C and are related to the particle-size distribution in the sample using Wadell's practical sedimentation formula tables.[15]

B. Water Analysis

1. Total Soluble Phosphorus. Filtered water samples were subjected to an ammonium persulfate digestion, and the amount of orthophosphate was then measured by forming the molybedum blue complex and utilizing the stannous chloride colorimetric method.[11]

2. Orthophosphate. The orthophosphate content of the filtered, undigested samples were measured by the stannous chloride colorimetric method.[11]

3. Total Alkalinity. An appropriate aliquot of each sample was titrated to the methyl red end-point with standard sulfuric acid.[11]

4. Nitrate. Nitrate concentrations were determined by reduction of nitrate-to-nitrite using amalgamated cadmium filings and diazotizing the nitrite with sulfanilamide and coupling with N-(1-naphyl)-ethylenediamine. The highly colored dye is measured colorimetrically and resulting absorbances are compared to the measured absorbances of nitrate standards carried through the same procedure.[11]

5. Total Kjeldahl Nitrogen. The unfiltered sample was digested with potassium sulfate, sulfuric acid, and mercuric sulfate as the digesting reagent. The ammonia concentration was then determined, either with an ammonia electrode (Orion) or by distillation into boric acid followed by nesslerization.[11]

6. Silica. Formation of the yellow molbdosilicic acid is carried out using acidic ammonium molybdate followed by its reduction to heteropoly blue using 1-amino-2-naphthol-4-sulfonic acid. The absorbance of the blue complex is measured at 815 nm and compared to the absorbances of standards.[11]

7. Chloride. An appropriate aliquot is titrated with mercuric nitrate using diphenylcarbazone as the indicator.

8. Sodium and Potassium. These metals were measured by flame emission using a Perkin-Elmer 306 atomic absorption spectrophotometer.

9. Calcium and Magnesium. Atomic absorption-flame analysis using a Perkin-Elmer 306 instrument was employed.

10. Zinc, Copper, Cadmium, Lead, Iron, Manganese, Aluminum, Chromium, and Nickel. The aqueous samples were filtered through 0.45-micron filters. The concentrations of the above metals were measured using the Perkin-Elmer 306 atomic absorption spectrophotometer, the Perkin-Elmer HGA 2100 graphite furnace, and a deuterium arc background corrector. For certain of the samples containing higher concentrations of iron, a colorimetric method was also used for soluble and particulate iron. These latter values are listed in Tables 24 through 26 along with the values obtained by atomic absorption analyses. For the colorimetric analysis, the iron is reduced to its ferrous state and reacted with bathophenanthroline to form a red compound which is extracted with iso-amyl alcohol. Particulate iron is computed from the difference in iron values between the filtered and unfiltered samples.[16]

11. Dissolved Oxygen. The azide modification of the Winkler Method was used.[11]

12. Total Phenolics. The river-water samples were collected in glass bottles and preserved with H_3PO_4 and $CuSO_4$ if not analyzed the same day. The samples were distilled, reacted with 4-aminoantipyrine. The absorbances of the chloroform extracts were measured at 460 nm and compared to the appropriate standards and blanks.[11]

13. Specific Conductance. The measurements were made in a water bath at 25°C using Freas-type conductivity cells and an Industrial Instruments Model RC16B Conductivity Bridge.

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